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STUDY OF THE REACTIONS OF THE POLYTHIONATES BY MEANS OF TAGGED SULFUR

II. REACTIONS OF THE TETRATHIONATES AND THE PENTATHIONATES

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In a previous work [1] the mechanism of some reactions of the formation and decomposition of trithionates was studied by means of radioactive sulfur, which was introduced into definite positions of the original substances. The data obtained for these reactions confirmed the ideas of D. I. Mendeleev [2], according to which polythionate molecules are composed of little unbranched chains of sulfur atoms with sulfite groups at the ends, and the principal reactions of formation and the reciprocal transformations of the polythionates proceed by means of displacements of the sulfite and thiosulfate groups.

In the present work the same isotopic method was used for the study of the reaction mechanisms and structure of the tetra- and pentathionates. This provided further confirmation of the indicated concepts.

Decomposition of tetra- and pentathionate. The distribution of tagged sulfur in the tetrathionate and pentathionate obtained was studied in all instances by determination of the activity of the products of their decomposition by potassium cyanide:

$$S_4O_6^{--} + 3CN^- + H_2O = S_2O_3^{--} + SO_4^{--} + CNS^- + 2HCN,$$

$$S_5O_6^{--} + 4CN^- + H_2O = S_2O_3^{--} + SO_4^{--} + 2CNS^- + 2HCN.$$

Both reactions took place rapidly and in exact accordance with these stoichiometric equations, owing to which they were recommended for analytical purposes [3]. The distribution of the activity between both sulfur atoms in thiosulfate was studied, also as it was earlier, by the hydrolytic decomposition of its silver salt:

$$S_2O_3^{--} + 2Ag^+ + H_2O = Ag_2S + SO_4^{--} + 2H^+.$$

The method of study of the activity distribution in polythionate employed here gave clear and well-defined results. All the central sulfur atoms (sulfide) of the chain were converted to thiocyanate and to the sulfide sulfur of thiosulfate (Ag_2S at the end), and all the sulfur atoms of the sulfite groups were converted to sulfate and to the sulfite group of thiosulfate (at the end, sulfuric acid). We were easily convinced of this from the data of Tables 1-4 by a comparison of the activity of the end products with that of the original sulfur.

The possibility of the distortion of the original activity distribution as a result of side reactions of the isotopic exchange of sulfur should be considered. From the literature it is known [4] that no exchange of sulfates was observed. We found that exchange between the thiocyanate and thiosulfate at room temperature was also absent after 26 hours, which considerably exceeded the time of our decomposition experiments and separation of its products. The exchange between thiosulfate and both polythionates takes place very rapidly [5], but only by exchange of the intact thiosulfate groups, and it cannot affect the activity distribution in the latter.

The absence of an exchange of sulfide sulfur atoms with sulfite (directly or via some intermediate step) was confirmed by the fact that, in all the experiments, the sulfate from the decomposition of polythionate and the sulfate from the decomposition of the final thiosulfate, were inactive.

The method of separation of the reaction products and of the measurement of their radioactivity was described earlier [1]. In all the experiments, unlike the previous works, we also measured the total activity of a portion of the thiosulfate isolated as benzidine sulfate, after oxidation (Carius). After precipitation of the thiosulfate and removal of the excess Ba^{++} ions by the addition of Na_2SO_4 until disappearance of the turbidity, the thiocyanate was precipitated by cupric sulfate. The thiocyanate precipatate contained an impurity of cyanide, but this did not affect the accuracy of the activity measurement, since it was also carried out after the oxidation of the thiocyanate (according to Carius).

TABLE 1

Tetrathionate from $\overset{*}{S}_2Cl_2 + SO_3^{--}$

Expt. No.	Activity (counts per 1 mg of S during 5 minutes)						Activity ratio				
	Original S (A)	Original S_2Cl_2 (B)	Tetrathionate (C)	Decomposition of tetrathionate**		Decomposition of final thiosulfate **	A/B	B/C	C/D	F/D	E/D
				Thiosulfate (D)	Thiocyanate(E)	Ag_2S (F)					
1a	8090	8020	4090	4060	7800	7930	1.01	1.96	1.01	1.95	1.92
1b*				4070	7950	7980			1.00	1.96	1.95
2a	4250	4390	2290	2150	4250	4220	0.97	1.92	1.06	1.96	1.98
2b*				2170	4230	4150			1.05	1.91	1.95
									Assumed		
							1	2	1	2	2

TABLE 2

Tetrathionate from $\overset{*}{S}SO_3^{--} + I_2$

Expt. No.	Activity (counts per 1 mg of S during 5 minutes)						Activity ratio				
	Original S (A)	Original $K_2S_2O_3$ (B)	Tetrathionate(C)	Decomposition of tetrathionate**		Decomposition of final thiosulfate **	A/B	B/C	C/D	F/D	E/D
				Thiosulfate (D)	Thiocyanate(E)	Ag_2S (F)					
1a	5210	2600	2530	2540	5200	5160	2.01	1.03	1.00	2.03	2.05
1b				2590	5230	5240			0.98	2.02	2.02
2a	4510	2250	2210	2220	4460	4430	2.00	1.02	1.00	2.00	2.01
2b				2210	4400	4520			1.00	2.04	1.99
									Assumed		
							2	1	1	2	2

Tetrathionate from sulfur monochloride and sulfurous acid. This reaction was predicted by D. I. Mendeleev [2], and was carried out only recently by Goehring and Stamm [6], who recommended it for the preparation of pure tetrathionate.

A solution of 4.5 g of tagged sulfur monochloride in 30 ml of petroleum ether [1], cooled to −15°, was added in small portions to a saturated solution of sulfurous anhydride in 45 ml of water cooled to 0°. Before addition of each subsequent portion the mixture was shaken until the disappearance of the yellow color. After separation of the ether layer, a current of air was passed through the aqueous layer until complete displacement of the free SO_2. After this, on cooling to 0°, the aqueous layer was neutralized with a solution of 9 g of KOH in 60 ml of alcohol. The potassium tetrathionate which precipitated was washed with alcohol and dried. After recrystallization from water at 60° it contained no other polythionates (qualitative reaction with $Hg_2(NO_3)_2$, ammoniacal solution of $AgNO_3$, etc.), sulfite, thiosulfate, sulfate and chloride.

As is evident from the data of Table 1, tetrathionate had 1/2 the activity of the original sulfur monochloride. It was all concentrated in the two central (sulfide) sulfur atoms, since the thiocyanate had the activity of the original sulfur, the sulfate from the decomposition of the tetrathionate was inactive, and the thiosulfate had the same activity as the tetrathionate, but the decomposition of this thiosulfate yielded inactive sulfate and a sulfide with the original activity. These ratios correspond to the following sulfur balance equations, in which the activity of the original sulfur was assumed to be equal to unity:

$$2\overset{1}{S} + Cl_2 = \overset{1}{S}_2Cl_2;\ \overset{1}{S}_2Cl_2 + 2\overset{0}{S}O_3^{--} = \overset{1}{S}_2(\overset{0}{S}O_3)_2^{--} + 2Cl^-.$$

* (In this and subsequent tables) Parallel experiments of tetrathionate decomposition.

** (In this and subsequent tables) The sulfate formed in all the experiments was inactive.

$$\overset{1}{S_2}\overset{0}{(SO_3)_2}^{--} + 3CN^- + H_2O = \overset{10}{SSO_3}^{--} + \overset{0}{SO_4}^{--} + \overset{1}{CNS}^- + 2HCN,$$

$$\overset{1}{SSO_3}^{--} + 2Ag^+ + H_2O = \overset{1}{Ag_2S} + \overset{0}{SO_4}^{--} + 2H^+.$$

Sulfur monochloride is the acid chloride of thiosulfurous acid, $S_2(OH)_2$, which does not exist in the free state, but gives rather stable symmetrical alkyl esters by reaction of sulfur monochloride with alcoholates [7]. Therefore, in the reaction considered it was assumed that thiosulfurous acid first formed, which then was converted to the tetrathionate by replacement of both hydroxyl groups by sulfites. This led to the observed distribution of active sulfur:

$$\overset{1}{S_2}Cl_2 + 2H_2O = \overset{1}{S_2}(OH)_2 + 2H^+ + 2Cl^-$$

$$\overset{1}{S_2}(OH)_2 + \overset{0}{2SO_3}^{--} + 2H^+ = \overset{1}{S_2}\overset{0}{(SO_3)_2}^{--} + 2H_2O.$$

This mechanism is in keeping with the mechanism proposed by the authors indicated [6], and in general outline it corresponds to D. I. Mendeleev's ideas [2]. The direct displacement of chlorine from S_2Cl_2 by the sulfite groups would also correspond to the activity distribution observed.

Tetrathionate from thiosulfate and iodine. This reaction, resting on the basis of an iodometric analysis, gives a high yield of pure tetrathionate. An aqueous solution of tagged potassium thiosulfate with radioactive sulfide sulfur was added dropwise, with stirring, to an alcoholic solution of iodine, cooled with ice [1]. The potassium tetrathionate which precipitated was washed carefully with alcohol until the removal of KI, and was then purified as described above.

It is evident from the data of Table 2 that it had the same average activity and the same distribution of active sulfur as did that obtained from sulfur monochloride and sulfite:

$$\overset{1}{S} + \overset{0}{SO_3}^{--} = \overset{10}{SSO_3}^{--}$$

$$\overset{10}{2SSO_3}^{--} + I_2 = \overset{1}{S_2}\overset{0}{(SO_3)_2}^{--} = 2I^-,$$

and further, as indicated above.

This reaction was recently studied, with the same results, by Aten [19], who used thiosulfate with tagged sulfite sulfur and decomposed the resulting tetrathionate with mercurous dichloride.

Thus, the reaction considered, in which iodine plays the role of an oxidizing agent, consists of the combination of two thiosulfate groups through sulfide sulfur atoms:

$$\overset{10}{2SSO_3}^{--} = {}^-\overset{0}{O_3}\overset{0}{S}\overset{1}{-}\overset{10}{SO_3}^- + 2e,$$

which also corresponds to the mechanism proposed by D. I. Mendeleev.

Tetrathionate from thiosulfate and sulfurous anhydride. Trithionate and tetrathionate were formed simultaneously by this reaction in the presence of catalytic quantities of arsenite. A study of the reaction by means of tagged sulfur was described in a previous work [1], but in it we investigated only the trithionate which formed. In order to verify the postulates proposed at that time concerning its mechanism, we repeated the experiments, studying the distribution of sulfur in the tetrathionate also (Table 3). As also earlier, the trithionate which formed had 1/4 of the activity of the original sulfur. It was found earlier that all of it was concentrated in the central (sulfide) sulfur atom. The tetrathionate had 3/8 of the original activity, all of it being concentrated in the two central (sulfide) sulfur atoms. This was evident from the fact that the sulfate from the decomposition of tetrathionate was inactive, but the thiosulfate had 3/8 of the original activity, all of which on its decomposition of the tetrathionate had 3/4 of the original activity:

$$\overset{3/4}{S}\overset{0}{SO_3}_{\ 2}^{--} + 3CN^- + H_2O = \overset{3/4}{S}\overset{0}{SO_3}^{--} + \overset{0}{SO_4}^{--} + \overset{3/4}{CNS}^- + 2HCN,$$

$$\overset{3/4}{S}\overset{0}{(SO_3)_2}^{--} + H_2O = \overset{3/4}{S}\overset{0}{SO_3}^{--} + \overset{0}{SO_4}^{--} + 2H^+,$$

$$\overset{3/4}{S}\overset{0}{SO_3}^{--} + 2Ag^+ + H_2O = \overset{3/4}{Ag_2S} + \overset{0}{SO_4}^{--} + 2H^+.$$

TABLE 3

Trithionate and Tetrathionate from $\overset{*}{S}SO_3^{--} + SO_2$

Expt. No.	Activity (counts per 1 mg S during 5 minutes)							Activity Ratio					
	Original S (A)	Original $Na_2S_2O_3$ (B)	Trithionate (H)	Tetrathionate (C)	Decomposition of tetrathionate **		Decomposition of final thiosulfate **	A/B	B/C	B/H	C/D	F/D	E/D
					Thiosulfate (D)	Thiocyanate (E)	Ag_2S (F)						
1a	7980	4110	2120	2880	2870	5660	5680	1.94	1.43	1.94	1.00	1.98	1.97
1b*					2970	5600	5710				0.97	1.92	1.89
2a	12900	6560	3180	4620	4620	8990	8830	1.97	1.42	2.06	1.00	1.91	1.95
2b*					4500	8720	8750				1.03	1.94	1.94
3a	12900	6560	3160	4720	4700	9040	9320	1.97	1.39	1.08	1.00	1.98	1.92
3b*					4640	9530	9370				1.02	2.02	2.05
4a	7090	3530	1810	2720	2740	5430	5400	2.01	1.30	1.95	1.03	1.97	1.98
4b*					2650	5360	5320				1.07	2.01	2.02
								Assumed					
								2	4/3	2	1	2	2

This activity distribution in both polythionates corresponds exactly to the mechanism proposed in the previous work, according to which sulfoxylic acid is first formed, which then gives pentathionate by the replacement of two hydroxyl groups by thiosulfate. A rapid successive replacement of one and two thiosulfate groups in the pentathionate by sulfite proceeds with the formation at first of tetrathionate, and later of trithionate:

$$\overset{1}{S} + \overset{0}{SO_3^{--}} = \overset{1\ 0}{SSO_3^{--}};\ \overset{1\ 0}{SSO_3^{--}} + 2H^+ + H_2O = \overset{1/2}{2S(OH)_2},$$

$$\overset{1/2}{S(OH)_2} + \overset{1\ 0}{2SSO_3^{--}} + 2H^+ = \overset{1/2\ 1\ 0}{S(SSO_3)_2^{--}} + 2H_2O,$$

$$\overset{1/2\ 1\ 0}{S(SSO_3)_2^{--}} + \overset{0}{SO_3^{--}} = \overset{0\ 1/2\ 1\ 0\ \ 1\ 0}{^-O_3SSSSSO_3^-} + \overset{1\ 0}{SSO_3^{--}},$$

$$2\overset{0\ 1/2\ 1\ 0\ \ 1\ 0}{^-O_3SSSSSO_3^-} + \overset{0}{2SO_3^{--}} = \overset{1/2\ 0}{S(SO_3)_2^{--}} + \overset{1\ 0}{S(SO_3)_2^{--}} + \overset{1\ 0}{SSO_3^{--}} + \overset{1/2\ 0}{SSO_3^{--}}.$$

Since both thiosulfate groups are equivalent, the observed average activity in the polythionates will be $\overset{3/4\ 0}{S_2(SO_3)_2^{--}}$ and $\overset{3/4\ 0}{S(SO_3)_2^{--}}$.

Thus, the investigation of tetrathionate gives a further demonstration of the validity of the mechanism of this reaction proposed earlier. In a previous paper [1] the inaccuracy of the concept of the mechanism proposed in a series of other works was indicated.

Pentathionate from thiosulfate and concentrated hydrochloric acid. The formation of pentathionate by the action of concentrated hydrochloric acid on thiosulfate in the presence of arsenite, observed by Salzer [8], was later studied in a series of works [10,11,12,16] and was employed for preparative purposes [9].

50 ml of concentrated hydrochloric acid was added in a slow stream to a solution of 33 g of tagged sodium thiosulfate in 40 ml of water, with the addition of 0.7 g of As_2O_3 dissolved in 50% NaOH. Both solutions were first cooled to −10°.

At the beginning of the reaction a great deal of H_2S was liberated, the quantity of which later was sharply decreased. After separation of the sodium chloride which came down, the mixture was left for 3-4 days at room temperature; at this time a small quantity of sulfur and arsenic sulfide precipitated. After separation of the latter the solution was evaporated in vacuo at 40° to a volume of 15 ml. The sodium chloride which came down again was removed, and 6.6 ml of glacial acetic acid and 5.4 g of potassium acetate (the latter as a paste, on preci-

tation by addition of glacial acetic acid to a saturated alcoholic solution of the acetate) were added to the solution at −10°. The acetate dissolved on shaking, and potassium pentathionate precipitated, which was recrystallized from 0.5 N hydrochloric acid and dried in a vacuum desiccator. No impurities of chloride, sulfide, sulfate and other polythionates were detected in it.

The results of measurement of the activity of the pentathionate and of the products of its decomposition by cyanide, are cited in Table 4.

TABLE 4

Pentathionate from $S^*SO_3^{--}$ + HCl

Expt. No.	Activity (counts per 1 mg of S during 5 minutes)								Activity ratio				
	Original S (A)	Original $Na_2S_2O_3$ (B)	Pentathionate (C)	Decomposition of pentathionate **		Decomposition of final thiosulfate **	By-products		A/B	B/C	D/C	F/D	E/D
				Thiosulfate (D)	Thiocyanate (E)	Ag_2S (F)	S (G)	As_2S_3 (I)					
1a	8790	4280	5060	4410	8610	8690	5880	5690	2.05	0.85	0.87	1.97	1.95
1b *				4370	-	8710	-	-			0.86	1.99	-
2a	7140	3730	4260	3710	7240	7310	5380	5000	1.99	0.88	0.87	1.97	1.95
2b *			4310	3720	7310	7390	5360	4840		0.87	0.86	1.98	1.96
3a	6660	3260	3930	3280	6420	6560	4770	4440	2.04	0.83	0.83	2.00	1.96
3b *				3290	6380	6720					0.84	2.04	1.94
											Assumed		
									2	5/6	5/6	2	2

The activity of the pentathionate was equal to 3/5 of that of the original sulfur, and it was all concentrated in the three central (sulfide) sulfur atoms; its decomposition yielded inactive sulfate, thiocyanate with the activity of the original sulfur, and thiosulfate with 1/2 of it, all of which on decomposition of this thiosulfate were converted to silver sulfide:

$$\overset{1}{S} + \overset{0}{SO_3^{--}} = \overset{10}{SSO_3^{--}},$$

$$5\overset{10}{SSO_3^{--}} + 4H^+ = \overset{1}{S_3}(\overset{0}{SO_3})_2^{--} + 2\overset{0}{SO_4^{--}} + \overset{2/3}{H_2S} + 2\overset{2/3}{S} + H_2O,$$

$$\overset{1}{S_3}(\overset{0}{SO_3})_2^{--} + 4CN^- + H_2O = \overset{10}{SSO_3^{--}} + \overset{0}{SO_4^{--}} + 2\overset{1}{CNS^-} + 2HCN,$$

$$\overset{10}{SSO_3^{--}} + 2Ag^+ + H_2O = \overset{1}{Ag_2S} + \overset{0}{SO_4^{--}} + 2H^+.$$

A definitive elucidation of the mechanism of this reaction requires further investigations. However, some general idea of it can be stated now. The role of arsenite, apparently, consists of the transfer of a sulfide sulfur atom from one thiosulfate molecule to two of its molecules, with the formation of pentathionate:

$$[As] + \overset{10}{SSO_3^{--}} = [As]\overset{1}{S} + \overset{0}{SO_3^{--}},$$

$$[As]\overset{1}{S} + 2\overset{10}{SSO_3^{--}} = {}^{-}\overset{0}{O_3}S\overset{1}{S}\overset{1}{S}\overset{10}{S}SO_3^- + [As],$$

where [As]S is the intermediate sulfide compound formed from arsenite and thiosulfate. Such a compound may be the complex ion $As(S_2O_3)_3^{---}$, the salt of which was isolated from a mixture of H_3AsO_3 + Na_2SO_4 [10,13]. It is unstable and is decomposed in an acid solution with the splitting off of sulfide sulfur. The formation of the As–S covalent bond must facilitate the breaking away of this sulfur from the thiosulfate. The catalytic action of arsenite might be accounted for by this.

We also measured the activity of the sulfur and of the arsenic sulfide which formed in a small quantity. For this, the elementary sulfur from their mixture was extracted with benzene, but the arsenic sulfide dissolved in sodium carbonate, after which both portions were oxidized (according to Carius). The activity of the arsenic sulfide was equal to 2/3 of the activity of the original sulfur (from 0.64 to 0.68), but for the sulfur was somewhat greater (from 0.69 to 0.74). It is known that in acid solutions the decomposition reaction of thiosulfate also proceeds with the formation of sulfur dioxide and hydrogen sulfide [10] (Vakenroder mixture). As was shown recently by means of tagged sulfur [14], this mixture reacts quantitatively with an excess of H_2S with the formation of water and sulfur, whereupon the latter contains 1/3 of the sulfur from SO_2 and 2/3 of the sulfur from H_2S, according to the equation:

$$\overset{0}{SO_2} + 2H_2\overset{1}{S} = \overset{2/3}{3S} + 2H_2O.$$

This sulfur must enter into exchange with the sulfur from $\overset{1}{As_2}S_3$, which leads to an equilibrium activity of both, found between 2/3 and 1 in fractions of the original activity, according to the experimental data.

Another possible explanation of the observed activity distribution in the sulfur and in the arsenic sulfide is the following: as usually assumed [15], hydrogen sulfide with sulfurous acid forms thiosulfurous acid which, reacting with hydrogen sulfide and with As^{+++}, gives sulfur and arsenic sulfide:

$$H_2\overset{1}{S} + H_2\overset{0}{SO_3} = \overset{1/2}{S_2}(OH)_2 + H_2O; \quad \overset{1/2}{S_2}(OH)_2 + H_2\overset{1}{S} = \overset{2/3}{3S} + 2H_2O,$$

$$\overset{1/2}{S_2}(OH)_2 + H_2\overset{1}{S} + 2As^{+++} = \overset{3/2}{As_2}S_3 + 2H_2O.$$

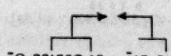
For the reaction considered, a mechanism via the intermediate formation of sulfur monoxide or sulfoxylic acid was proposed in different works [10,11], which did not agree with the activity distribution which we found, since this mechanism would probably introduce into the polythionate, sulfide sulfur with 1/2 the original activity. According to the same considerations the mechanisms via the intermediate formation of radical-ions [12], and the often mentioned scheme of Basset and Durrant [16], with the consecutive addition of sulfur atoms to the trithionate first formed, are incorrect.

Structure and Reactions of Polythionates

From the results obtained in both works, a series of general conclusions may be reached concerning the structure and reactions of the polythionates. In all the reactions which we studied, two valence states of the sulfur atom are clearly isolated--the sulfite (sexivalent), entering into both sulfite groups of the polythionate, and the sulfide (bivalent), connecting these sulfite groups. The formation of the polythionates proceeds by the addition of sulfite or thiosulfate groups to the sulfide sulfur of the original substances. Reciprocal transformations of the polythionates also were carried out by transfer of these groups from one of the sulfide sulfur atoms to another, but not by transfer of the sulfur atoms broken away from the polysulfide chain or adding to it, as has been assumed for the most part. For example, we usually considered the disproportionation reaction, $2S_4O_6^{--} = S_3O_6^{--} + S_5O_6^{--}$, as two consecutive steps:

$$S_4O_6^{--} = S + S_3O_6^{--}; \quad S_4O_6^{--} + S = S_5O_6^{--},$$

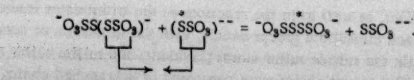
whereas, in reality, an exchange of sulfite and thiosulfate groups occurs in such reactions as:



$$^-O_3SS(SSO_3)^- + {}^-(O_3S)SSSO_3^- = {}^-O_3SSSO_3^- + {}^-O_3SSSSSO_3^-.$$

This follows from our data, and also from the results of several other recent works [6,17,19] with the application of tagged sulfur.

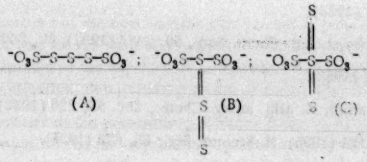
In reactions with thiosulfate, which also according to its chemical nature belongs to the thionates, no exchange of groups was observed by ordinary chemical methods, but it was observed by isotopic exchange of sulfur [5], for example:



In the reactions which we studied, the thiosulfate had the same isotopic composition as the thiosulfate groups in polythionate; therefore, no such exchange altered the distribution of active sulfur. On the other hand, the agreement of the isotopic composition of the original and final thiosulfate in these reactions served as a further confirmation of the concepts considered.

It follows from them that the polythionates are constructed from little unbranched chains of sulfide sulfur atoms, with sulfite groups at the ends (A).

Incorrect ideas concerning the reactions of the polythionates, by the breaking loose of sulfur atoms from the little chains or by their introduction into the little chains, led in a series of new works, to the hypothesis of a branched chain (B) or (C) [18], which was devoid of basis.



Apparently, these ideas on the structure and reactions of the polythionates can also be extended to hexathionate. The higher polythionates with a number of sulfur atoms greater than six have still been little studied, and isotopic methods have not been applied to them, so that the problem of their structure requires additional investigation.

In some decomposition reactions of the polythionates a deeper change occurs, with the displacement of elementary sulfur atoms, occurring apparently, as a result of secondary transformations of the products of decomposition of the polythionates. Such reactions, like the complex processes in the Vakenroder liquid, require further study.

The general considerations cited, based on the study of the reactions of the polythionates by means of tagged sulfur, correspond completely to the ideas proposed by D. I. Mendeleev [2] in 1870, which are considered in greater detail in a paper by one of us [20]. Subsequently the ideas of D. I. Mendeleev were not used much and various schemes of the reactions of the polythionates and their structures were proposed, based only on a study of the final products and those intermediate compounds which they were able to isolate. This led to contradictory and erroneous ideas in a number of works.

SUMMARY

1. Some typical reactions of the formation and decomposition of tetrathionate and pentathionate were studied with the application of tagged sulfur.

2. In the production of tetrathionate from sulfur monochloride and sulfurous acid both chlorine atoms are replaced by sulfite groups, probably with the intermediate formation of thiosulfurous acid.

3. In the production of tetrathionate from thiosulfate and iodine, a combination of the two thiosulfate atoms occurs, with the formation of a bond between both sulfide sulfur atoms. Iodine plays the role of oxidizing agent in this reaction.

4. In the production of tetrathionate from thiosulfate and sulfurous anhydride, in the presence of arsenous acid, sulfoxylic acid forms first, in which the hydroxyl groups are later replaced by thiosulfate and sulfite groups, which leads to the subsequent formation of pentathionate, tetrathionate and trithionate.

5. In the formation of pentathionate by the decomposition of thiosulfate with hydrochloric acid in the presence of arsenous acid, the combination of two thiosulfate groups with a sulfur atom occurs with the cutting off of arsenite from the third thiosulfate group.

6. In all these reactions, as well as in the reactions of the trithionates studied earlier by the same method, a transfer of all the sulfite and thiosulfate groups occurs, with the formation or decomposition of bonds between them and the sulfide sulfur, while the sulfide sulfur atoms (bivalent) and sulfite sulfur atoms (sexivalent) retain their characteristic functions. The polythionates were composed of unbranched chains of sulfide sulfur with sulfite groups at the ends.

7. The results obtained confirm completely the theory of the polythionates proposed by D. I. Mendeleev in 1870.

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INVESTIGATION IN THE FIELD OF THE BASIC CHLORIDES OF IRON

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Literature data on the oxychlorides of iron are very numerous and inconsistent. Without stopping for a critical review of these data, we cite only data on the chemical composition of the oxychlorides described [1].

$FeOCl$	$2FeCl_3 \cdot 5Fe_2O_3$
$FeOCl \cdot Fe_2O_3$	$2FeCl_3 \cdot 6Fe_2O_3 \cdot 9H_2O$
$FeOHCl_2$	$2FeCl_3 \cdot 9Fe_2O_3$
$FeOCl_4$	$2FeCl_3 \cdot 12Fe_2O_3$
$2FeCl_3 \cdot 2Fe_2O_3 \cdot 3H_2O$	$2FeCl_3 \cdot 17Fe_2O_3$
$2FeCl_3 \cdot 3Fe_2O_3$	$2FeCl_3 \cdot 72Fe_2O_3$

Data on the existence and composition of the oxychlorides which occur as products of the hydrolysis of solutions of iron salts are especially numerous and are the most contradictory. Different methods were employed by the authors in the investigations: direct determination of the oxychloride composition by chemical analysis, nephelometry, conductometry, potentiometry, pH determination, determination of the diffusion rate, etc.

In our opinion, the colloidal structure of the preparations obtained is the chief source of the difficulties encountered in the determination of the composition of the oxychlorides, particularly in the determination of the composition of the hydrolysis products of iron salts. By none of the methods listed above was it possible to take into account the colloidal structure of the objects under investigation. Meanwhile, the disregarding of the properties of the colloidal phases, as was demonstrated by numerous facts, led in many instances to incorrect, distorted results of the investigation. G. B. Fridman [2] attempted to take into account the characteristics of the colloidal structure of the oxychlorides, using for the investigation the method of a fourth component [3].

As a result of an investigation of the ferric chloride hydrolysis products obtained at 50° and at room temperature, Fridman found an oxychloride, the composition of which in his opinion corresponded to the formula $2FeCl_3 \cdot 1.5[Fe_2O_3 \cdot 2.5H_2O]$. It is impossible to consider these data on the composition of the oxychloride as correct, because of the fact that on the basis of the method of investigation used, an error was incurred, which could not be indicated in the results of the analysis.

Data of the investigation of systems of $Fe_2O_3-FeCl_3-H_2O-CaCl_2$ by the inert component method are cited in the present report. The solid phase in these systems consists of the ferric chloride hydrolysis products, obtained at room temperature.

EXPERIMENTAL

System I. $Fe_2O_3 - FeCl_3 - H_2O - CaCl_2$

The pure salt $FeCl_3 \cdot 6H_2O$ was dissolved in water until a one percent solution was obtained. The first signs of turbidity of the solution were observed after 4 days. The intensity of the turbidity gradually increased, yet the precipitate did not settle to the bottom but was in the suspended state, and the solution did not clarify. After 4 months, 2 liters of 20% $CaCl_2$ was added to 20 liters of the solution, as a result of which complete sedimentation set in after two days. It was possible to separate the precipitate from the mother liquor only by a very careful decantation. With a little shaking, peptization took place, and only on the following day was the liquid clarified. For a more complete separation from the mother liquor, the precipitate was transferred to filter paper and then squeezed under the press.

The resulting preparation was washed with a solution of an inert component – 10% $CaCl_2$ – in order to remove the adsorbed $FeCl_3$ from the surface of the preparation and from the liquid phase. Washing was carried out by decantation over a period of a month: after every 2 hours the first week, and 2 times a day for the rest of the time. The iron content was checked by the intensity of the color of 10 ml of the wash liquid on addition to it of two drops of a potassium ferrocyanide solution.

The washed preparation was divided into portions and placed in prepared samples of solutions of different concentrations of the inert component, $CaCl_2$. In order to establish the adsorption equilibrium the samples were kept for a month, after which they were analyzed. At the time of analysis the age of the preparation was 6 months. For the analysis weighed portions of the liquid phase and residues, i.e., solid phases together with the portion of mother liquor adhering to them, were withdrawn simultaneously from each sample. The content of $CaCl_2$, and also of Fe_2O_3, in the liquid phases was determined. The Fe_2O_3 content in the liquid phases proved to be so small (it did not exceed 0.1%) that it could not be taken into account, considering the degree of accuracy of the indirect determinations. The $CaCl_2$, Fe_2O_3 and $FeCl_3$ content in the residues was determined.

The iron content was determined gravimetrically as ferric oxide, the chlorine content as AgCl, the calcium content – by precipitation as calcium oxalate, and in duplicate samples – permanganatometrically.

By calculation of the analytical data the total calcium found was combined with chlorine, the excess of chlorine was combined with iron, the excess iron was converted to Fe_2O_3.

The analytical data are cited in Table 1.

A composition – state – concentration diagram was constructed (Fig. 1) from the analytical data. This diagram was an orthogonal projection of a three-dimensional figure – a right-angled tetrahedron – onto the horizontal and vertical planes. On the upper part of the diagram was the vertical oyx plane of the plotted points expressing the composition of the liquid phases ($CaCl_2$ content) and of the residues ($CaCl_2$ and Fe_2O_3 content). Straight lines were drawn through the composition points of the liquid phases and residues until they intersected. On the diagram (Fig. 1) these straight lines of the residue compositions intersected at one point, E_1. The common point of intersection of the straight lines corresponds to the presence in the system of a solid phase which is an individual chemical compound. This point E_1 also showed that in the system the practical value of the limiting adsorption of the inert component $CaCl_2$ is reached. The coordinates of point E_1 correspond to the Fe_2O_3 and $CaCl_2$ content in the solid phase. On the lower part of the diagram – the horizontal oxz plane – were plotted the points corresponding to the Fe_2O_3 and $FeCl_3$ contents in the solid phase. In the lower part of the diagram the coordinates of the composition points of the liquid phases coincided with the origin of the coordinates, since the Fe_2O_3 and $FeCl_3$ content in the liquid phases is practically equal to zero. A straight line was drawn from the origin of the coordinates through the composition points of the residues. The point of intersection of this line with the straight line drawn through point E_2 parallel to the ordinate axis, and corresponding to the Fe_2O_3 and $FeCl_3$ content in the solid phase, was E_1. The water content was found by difference: $H_2O = 100-(FeO_3\% + FeCl_3\% + CaCl_2\%)$.

Calcium chloride did not enter stoichiometrically into the composition of the solid phase, but was sorbed by it. Its content in the solid phase determined the adsorption capacity of this phase. The value of the practical limiting adsorption of $CaCl_2$, attained on the solid-liquid surface of separation, also served in the present case as an external expression of the colloidal state of the phase at the moment of analysis.

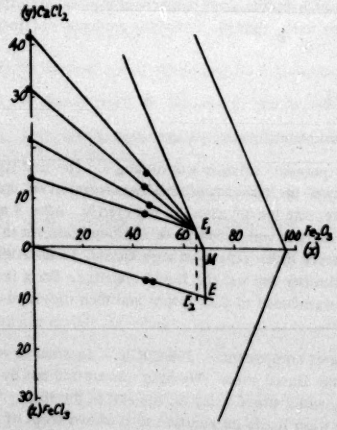

Fig. 1. Composition – state – concentration diagram of System (I) $Fe_2O_3-FeCl_3-H_2O-CaCl_2$.

TABLE 1

Analytical Data of System I

Sample	liquid phase (in %)		Residue (in %)		
No.	$CaCl_2$	Fe_2O_3	$CaCl_2$	$FeCl_3$	Fe_2O_3
1	42.28	Traces	14.32	6.87	46.96
2	31.99	Traces	11.67	6.73	46.45
3	21.58	Traces	8.27	6.92	47.71
4	13.38	Traces	6.28	6.70	47.51

The composition of the solid phase could be found graphically, and also by calculation from analytical data.

In order to find the composition of the solid phase graphically from point y, which corresponds to 100% of the inert component, we drew a straight line through the point of intersection of the straight lines of composition E_1 of the residues until it intersected with the abscissa (point M). From point M we erected a perpendicular to its intersection at Point E with the straight line drawn from the origin of the coordinates through

Point E_2. The coordinates of Point E also express the Fe_2O_3 and $FeCl_3$ content in the solid phase. The H_2O content was found by difference, subtracting from a hundred the sum of the contents of the components found.

The determination of the composition of the solid phase by the method of calculation led to the solution of a system of equations of a family of straight lines which passed through two given points and intersected at a third common point in the area.

As a result of the investigation the data on the composition of the solid phase, found both graphically and by analytical calculation, agreed. These data showed that the solid phase found in the system contains in its composition, besides ferric oxide and water, also ferric chloride. The following were found: Fe_2O_3 65.35%, $FeCl_3$ 9.48%, $CaCl_2$ 3.38%, and H_2O 21.79%. The composition of the solid phase may be expressed by the chemical formula: $7Fe_2O_3 \cdot FeCl_3 \cdot 21H_2O$.

System II. $Fe_2O_3 - FeCl_3 - H_2O - CaCl_2$

The solid phase in this system was prepared similarly to that in System I, and differed from it only in age. The preparation was under a layer of the inert component in hermetically sealed vessels for 18 months. The analytical determinations were carried out just as for System I. The analytical data are cited in Table 2.

From the analytical data, a diagram was constructed (Fig. 2), where the state of the solid phase was expressed by the value of the practical limiting adsorption of the inert component, $CaCl_2$. On this diagram the straight lines of the residue compositions also had one specific point of intersection, which indicated the attainment of the practical limiting adsorption of the inert component on the surface of the solid phase. As a result of the calculation of the composition of the liquid phase the following were found: Fe_2O_3 71.95%, $FeCl_3$ 9.12%, $CaCl_2$ 2.45%, and H_2O 16.48%.

This composition corresponds to the formula: $8Fe_2O_3 \cdot FeCl_3 \cdot 16H_2O$.

TABLE 2

Analytical Data of System II

Sample No.	Liquid Phase (in %)		Residue (in %)		
	$CaCl_2$	Fe_2O_3	$CaCl_2$	$FeCl_3$	Fe_2O_3
1	24.72	Traces	9.02	6.41	50.71
2	21.56	Traces	8.24	6.35	50.18
3	17.52	Traces	6.92	6.43	50.63
4	14.41	Traces	5.75	6.64	52.06

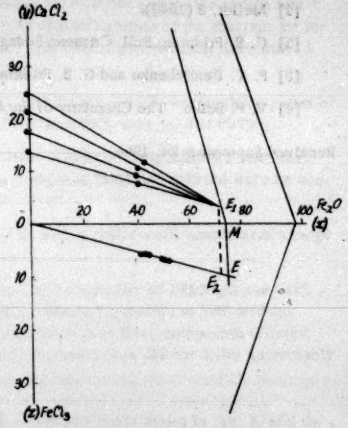

Fig. 2. Composition – state – concentration diagram of System (II) $Fe_2O_3 - FeCl_3 - H_2O - CaCl_2$.

DISCUSSION OF RESULTS

Investigation of the system $Fe_2O_3 - FeCl_3 - H_2O - CaCl_2$ of two ages showed that the solid phases were the hydrolysis products of ferric chloride, which were composed of both ferric oxide and water, and also ferric chloride. The resulting data showed that the composition of the ferric oxychloride cited by Fridman was erroneous. In the production of the preparation, which we investigated in System I, the conditions under which Fridman's preparation was obtained were reproduced; however, his results proved to be not reproducible. As was already indicated, the error incurred on the basis of the method of the fourth component, which Fridman used, was the reason for this. In the liquid phase, in the system $Fe_2O_3 - FeCl_3 - H_2O - CaCl_2$, there were two components besides water: a third, $FeCl_3$, and a fourth $CaCl_2$ (inert). The role of the fourth component, $CaCl_2$, amounts to the fact that it is adsorbed by the solid phase, and it displaced molecules of the other components of the system (chiefly $FeCl_3$ molecules) from the adsorption layer and obstructed the surface of the solid phase. However, Fridman did not consider that, in addition, a negative adsorption of ferric chloride must arise, since it was displaced from the adsorption layer.

In the analysis of the residues of each sample, the negative adsorption value must lead to a lowering of the results of the determination of the ferric chloride content, which was also confirmed by the data obtained by Fridman.

The ferric chloride hydrolysis products underwent changes during the aging process. The value of the practical limiting adsorption of the inert component, $CaCl_2$, at the surface of the solid phase, changed. A change of the $CaCl_2$ content from 3.4 to 2.6% showed that during the interval between the two analyses (12 months) processes of decrease of the degree of dispersion and increase of the degree of order, which also led to a decrease of the adsorption capacity, proceeded in the solid phase. This change of state of the colloidally-dispersed phase led to the splitting off of water, i.e., led to a decrease of the degree of hydration. We also observed a decrease of the degree of hydration during the aging process of the residues for other objects of investigation [4]. In addition, a decrease of the quantity of $CaCl_2$ and water also decreases the $FeCl_3$ content. The latter circumstance may serve as a criterion of the fact that the preparations studied were solid solutions. However, the resulting composition–state–concentration diagrams were typical of the individual compounds.

SUMMARY

1. The system Fe_2O_3–$FeCl_3$–H_2O–$CaCl_2$ with solid phases – ferric chloride hydrolysis products which differed in age (6 and 18 months) – was investigated.

2. The composition of the hydrolysis products, which may be expressed by the chemical formulas, $7Fe_2O_3 \cdot FeCl_3 \cdot 21H_2O$ and $8Fe_2O_3 \cdot FeCl_3 \cdot 16H_2O$, was established.

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REACTION OF LEAD TITANATE WITH SODIUM AND POTASSIUM SILICATES

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The problem of the nature of the Seignette-electric and piezo-electric properties of lead titanate has attracted the attention of physicists and chemists [1-3] and has introduced the necessity of a close study of the properties of monocrystalline lead titanate.

The dielectric properties and the blast furnace structure of lead titanate monocrystals obtained from the fusion of PbO, V_2O_5 and TiO_2 were described in the literature [4,5].

The results of an investigation of the reaction of lead titanate with sodium and potassium silicates in melts, for the purpose of an investigation of the feasibility of growing $PbTiO_3$ monocrystals from the melt, are cited in the present paper.

EXPERIMENTAL

An investigation of the Na_2SiO_3–$PbTiO_3$–K_2SiO_3 system was carried out by the visual-polythermal fusibility method. Since melts of sodium and potassium silicates are viscous and have a tendency toward super-cooling, the determination of the temperature of appearance of the first crystals was carried out by means of repeated heating and cooling of the melts, with required introduction of a priming device. It should be noted that sodium silicate crystallizes much more readily than does potassium silicate, and the investigation of the part of the system which was enriched in sodium silicate presents no particular difficulty. The most difficult portion of the diagram for investigation was that enriched in potassium silicate, but also in this region the viscosity of the melt decreases in proportion to the extent of the increase of the lead titanate concentration.

The sodium and potassium silicates used for the work were of "pure analytical quality", with melting points of 1082° for Na_2SiO_3 and 970° for K_2SiO_3.* Calculated, weighed portions of PbO and TiO_2 were used as $PbTiO_3$.

Binary sides (Table 1, Fig. 1). Na_2SiO_3–$PbTiO_3$ was a eutectic system. K_2SiO_3–$PbTiO_3$ formed a chemical compound close to the composition $3K_2SiO_3 \cdot 2PbTiO_3$. The crystalline compound indicated differed from its components, and melted at 787° without decomposition.

In one of the previous works [7] the present system was investigated through a rather small concentration range (5%), and therefore also remained incompletely examined.

Na_2SiO_3–K_2SiO_3, according to the literature [8], is a eutectic system, with a eutectic at 15% Na_2O and 745°. We established two chemical compounds, close in composition to $3K_2SiO_3 \cdot 2Na_2SiO_3$ (melted at 796° without decomposition), and $3K_2SiO_3 \cdot Na_2SiO_3$, which melted at 793°. The crystallization of these compounds differed from that for sodium and potassium silicates; however, the nature of their crystallization did not differ appreciably.

The System Na_2SiO_3–K_2SiO_3–$PbTiO_3$

12 sections through the system were investigated. The distribution of the sections is shown in Fig. 2, and the data are cited in the composite Table 2 and in Figs. 3 and 4.

The boundary of the regions of crystallization of sodium silicate and of the compound $3K_2SiO_3 \cdot 2PbTiO_3$ was specified by Sections 1-4 by the sections with a Na_2SiO_3–K_2SiO_3 side in the direction of $PbTiO_3$, these fixed the boundary of the same regions with the regions of $PbTiO_3$, K_2SiO_3, $3K_2SiO_3 \cdot 2Na_2SiO_3$ and $3K_2SiO_3 \cdot Na_2SiO_3$. The Sections 1-4** consisted only of the branches of the compounds $3K_2SiO_3 \cdot 2PbTiO_3$ and Na_2SiO_3. The sodium silicate in this region of the system crystallized much better than did pure Na_2SiO_3; even without the introduction of seed crystals the sodium silicate, on cooling the melts indicated, crystallized as rectangular tablets without appreciable supercooling.

* According to the data [6], the melting point of Na_2SiO_3 is 1088° and of K_2SiO_3 is 976°.

** Section 4 in the range of several per cents passes through the $PbTiO_3$ region; however, we did not determine the point of intersection of the regions of $PbTiO_3$ and of the compound, and the $PbTiO_3$ branch was not indicated in Fig. 3.

TABLE 1

1st Column – Mole% of Added Substance, 2nd Column – Temperature of Appearance of First Crystals

1	2
K_2SiO_3–$PbTiO_3$	
3	932°
6	884
9	836
12	800
15	780
18	750
21	694
24	694
27	727
30	751
33	770
36	780
39	783
42	783
47	800
48	822
E_1 at 22.5% $PbTiO_3$ and 674°;	
E_2 at 46% $PbTiO_3$ and 782°.	

1	2
Na_2SiO_3–K_2SiO_3	
20	954°
30	874
35	860
36	844
40	828
42	814
45	800
48	792
51	784
54	788
57.5	793
60	793
61	788
63	777
64	772
66	778
67.5	780
69	785
70	788
73	795
75	795
79	781°
82	753
85	772
88	800
91	834
94	863
E_1 at 51% K_2SiO_3 and 784°;	
E_2 at 63.5% K_2SiO_3 and 768°;	
E_3 at 82% K_2SiO_3 and 753°.	
Na_2SiO_3–$PbTiO_3$	
15	985°
20	958
25	931
30	903
35	857
40	908
45	961
50	992
55	1032
E at 35% $PbTi_3$ and 857°.	

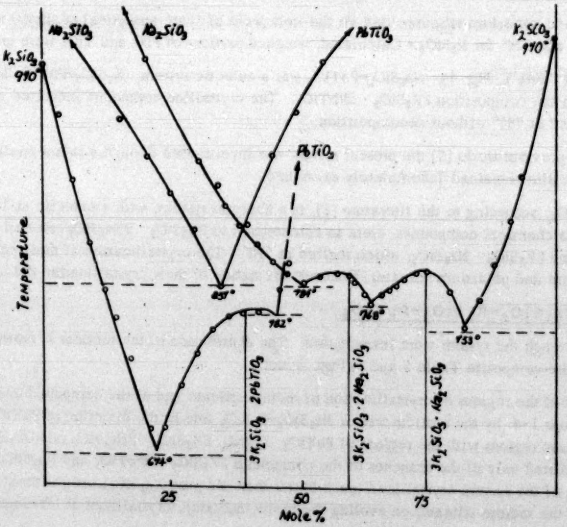

Fig. 1. Binary sides of profile Na_2SiO_3–$PbTiO_3$–K_2SiO_3

• E is a eutectic.

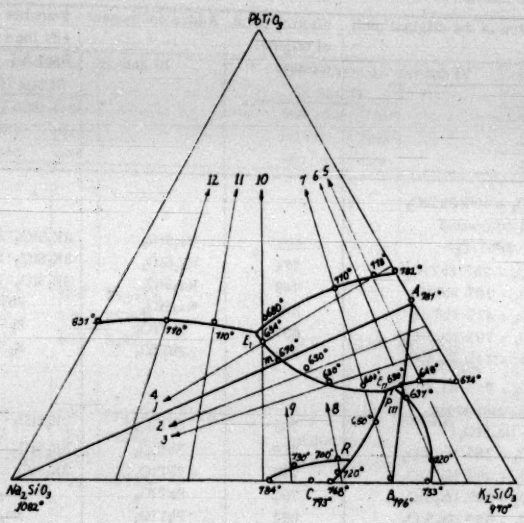

Fig. 2. Distribution of the sections through the surface of crystallization of the profile Na_2SiO_3–$PbTiO_3$–K_2SiO_3.

A) Polar compound $3K_2SiO_3 \cdot 2PbTiO_3$; B) polar compound $3K_2SiO_3 \cdot Na_2SiO_3$; C) polar compound $3K_2SiO_3 \cdot 2Na_2SiO_3$.

Section 1 of the polar compound $3K_2SiO_3 \cdot 2PbTiO_3$ in the direction of Na_2SiO_3 was of the nature of a binary system with a eutectic point at 670°. The latter was a reversal within the system. This follows from a projection of the crystallization lines of the system onto the Na_2SiO_3–K_2SiO_3 side (Fig. 6). In Fig. 5 the complete surface of crystallization of the system Na_2SiO_3–$PbTiO_3$–K_2SiO_3 is shown. It consisted of six regions, the names and sizes of which are cited in Table 3.

DISCUSSION OF RESULTS

The system Na_2SiO_3–$PbTiO_3$–K_2SiO_3 was a stable profile of the complex multi-component system Na, K, Pb || SiO_3, TiO_3, represented graphically as a prism (Fig. 7). •

The secondary sides Na_2SiO_3–$PbTiO_3$ and K_2SiO_3–$PbTiO_3$ of the present profile were in their turn diagonal profiles of the ternary reciprocal systems Na, Pb || SiO_3, TiO_3 and K, Pb || SiO_3, TiO_3 of the lateral boundaries of the prism indicated.

The fact that the profile Na_2SiO_3–$PbTiO_3$–K_2SiO_3 is stable follows from the fact that its secondary sides bear the character of binary systems. Thus, the system Na_2SiO_3–$PbTiO_3$ was a eutectic. In the system K_2SiO_3–$PbTiO_3$ the binary compound $3K_2SiO_3 \cdot 2PbTiO_3$ formed. The presence of a binary compound was confirmed by the fusibility diagram of the K_2SiO_3–$PbTiO_3$–Na_2SiO_3 profile. Thus, the section proceeding from the pole of the compound indicated in the direction of Na_2SiO_3 bears the character of a binary system, the eutectic point of which is a reversal point (Figs. 5, 6).

• In Fig. 7 the profile studied is crosshatched.

TABLE 2

Specific Points of the Internal Sections of the System

Sections	Composition of the original melt	Melting point of original mixture	Added component	Branches of crystallization curves and their intersections		
				Branch I	Intersection of I and II	
					% of added substance *	temperature
1	60% K_2SiO_3 + 40% $PbTiO_3$ (Terminal compound $3K_2SiO_3 \cdot 2PbTiO_3$)	787°	Na_2SiO_3	$3K_2SiO_3 \cdot 2PbTiO_3$	35.0	670°
2	65% K_2SiO_3 + 35% $PbTiO_3$	774	Na_2SiO_3	$3K_2SiO_3 \cdot 2PbTiO_3$	26.5	650
3	70% K_2SiO_3 + 30% $PbTiO_3$	748	Na_2SiO_3	$3K_2SiO_3 \cdot 2PbTiO_3$	26.0	630
4	53% K_2SiO_3 + 47% $PbTiO_3$	802	Na_2SiO_3	$PbTiO_3$	not determined	
5	90% K_2SiO_3 + 10% Na_2SiO_3	830	$PbTiO_3$	K_2SiO_3	22.0	648
6	86% K_2SiO_3 + 14% Na_2SiO_3	772	$PbTiO_3$	K_2SiO_3	4.0	720
7	75% K_2SiO_3 + 25% Na_2SiO_3 (Terminal compound $3K_2SiO_3 \cdot Na_2SiO_3$)	796	$PbTiO_3$	$3K_2SiO_3 \cdot Na_2SiO_3$	12.0	650
8	65% K_2SiO_3 + 35% Na_2SiO_3	770	$PbTiO_3$	$3K_2SiO_3 \cdot Na_2SiO_3$	2.0	720
9	55% K_2SiO_3 + 45% Na_2SiO_3	790	$PbTiO_3$	$3K_2SiO_3 \cdot 2Na_2SiO_3$	2.5	730
10	50% K_2SiO_3 + 50% Na_2SiO_3	790	$PbTiO_3$	Na_2SiO_3	29.5	654
11	35% K_2SiO_3 + 65% Na_2SiO_3	860	$PbTiO_3$	Na_2SiO_3	35.0	710
12	20% K_2SiO_3 + 80% Na_2SiO_3	956	$PbTiO_3$	Na_2SiO_3	35.5	770

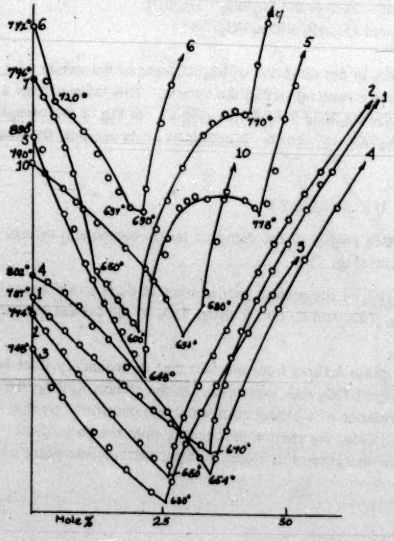

Fig. 3. Sections through the system Na_2SiO_3 – $PbTiO_3$ – K_2SiO_3.

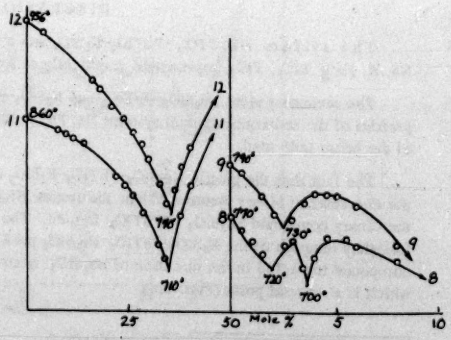

Fig. 4. Sections through the system Na_2SiO_3 – $PbTiO_3$ – K_2SiO_3.

* Equimolar percentages everywhere.

Branch II	Intersection of II and III		Branch III	Intersection of III and IV		Branch IV	Intersection of IV and V		Branch V
	% of added substance	temperature		% of added substance	temperature		% of added substance	temperature	
Na_2SiO_3									
Na_2SiO_3									
Na_2SiO_3									
$3K_2SiO_3 \cdot 2PbTiO_3$	35.0	654°	Na_2SiO_3						
$3K_2SiO_3 \cdot 2PbTiO_3$	45.0	778	$PbTiO_3$						
$3K_2SiO_3 \cdot Na_2SiO_3$	18.5	637	K_2SiO_3	22.0	630°	$3K_2SiO_3 \cdot 2PbTiO_3$	not determined		$PbTiO_3$ *
Na_2SiO_3	21.0	600	$3K_2SiO_3 \cdot PbTiO_3$	43.0	770	$PbTiO_3$	not determined		
$3K_2SiO_3 \cdot 2Na_2SiO_3$	3.6	700	Na_2SiO_3	not determined					
Na_2SiO_3	not determined			not determined					
$3K_2SiO_3 \cdot 2PbTiO_3$	33.5	680	$PbTiO_3$						
$PbTiO_3$									
$PbTiO_3$									

* Intersection not determined.

TABLE 3

Region	Region of crystallization	Area of region (in % of the total surface of the system)
1	$PbTiO_3$	37.86
2	Na_2SiO_3	37.42
3	K_2SiO_3	5.85
4	$3K_2SiO_3 \cdot 2PbTiO_3$	12.94
5	$3K_2SiO_3 \cdot Na_2SiO_3$	4.96
6	$3K_2SiO_3 \cdot 2Na_2SiO_3$	0.97

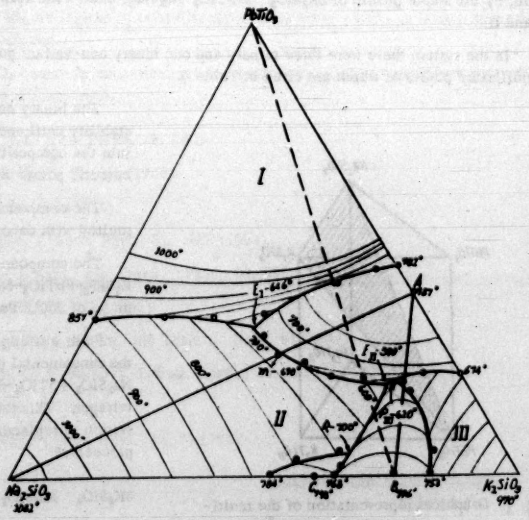

Fig. 5. Total surface of crystallization of the system Na_2SiO_3–$PbTiO_3$–K_2SiO_3.
A), B) and C) are the same symbols as were designated for Fig. 2.

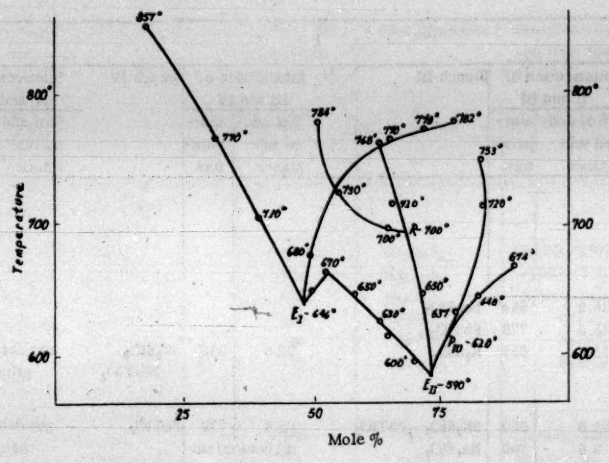

Fig. 6. Projection of lines of joint crystallization of the Na_2SiO_3–$PbTiO_3$–K_2SiO_3 profile onto the Na_2SiO_3–K_2SiO_3 side.

A triangulation of the system was carried out for the two profiles, shown in Fig. 5 by the heavy lines. By the unstable profile $3K_2SiO_3 \cdot Na_2SiO_3$–$3K_2SiO_3 \cdot 2PbTiO_3$ the system Na_2SiO_3–K_2SiO_3–$PbTiO_3$ was divided into the phase triangle III and the tetragon Na_2SiO_3–$PbTiO_3$–$3K_2SiO_3 \cdot 2PbTiO_3$–$3K_2SiO_3 \cdot Na_2SiO_3$. The latter in its turn, by the stable profile of $3K_2SiO_3 \cdot 2PbTiO_3$–Na_2SiO_3, underwent triangulation to the subordinate ternary systems I and II.

In the system there were three ternary and one binary non-variant point, the character, composition and equilibrium phases of which are cited in Table 4.

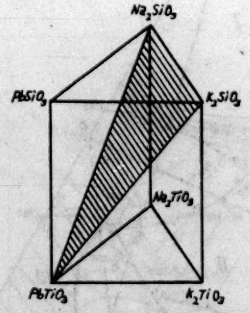

Fig. 7. Graphical representation of the multi-component system Na,K,Pb ‖ SiO_3,TiO_3.

The binary compound $3K_2SiO_3 \cdot 2PbTiO_3$ retained its stability until complete cooling of the system, entering into the composition of the phase complexes at the eutectic points E_I and E_{II}.

The compound $3K_2SiO_3 \cdot Na_2SiO_3$ inside the system melted with decomposition.

The compound $3K_2SiO_3 \cdot 2Na_2SiO_3$ in the profile K_2SiO_3–$PbTiO_3$–Na_2SiO_3 exists only at Point R with a m. p. of 700°. Point R is a binary slope point.

From a triangulation of the system it follows that the fundamental chemical process occurs in the Na_2SiO_3–$PbTiO_3$–$3K_2SiO_3 \cdot 2PbTiO_3$–$3K_2SiO_3 \cdot Na_2SiO_3$ tetragon. This tetragon is a ternary irreversibly-reciprocal system of replacement [9], in which the following reaction proceeds:*

$$3K_2SiO_3 \cdot Na_2SiO_3 + 2PbTiO_3 \rightarrow 3K_2SiO_3 \cdot 2PbTiO_3 + Na_2SiO_3.$$

* Unstable profile in the tetragon was shown in Fig. 5 by dotted lines.

TABLE 4

Composition and Equilibrium Phases of Nonvariant Points of the System

Nature of points	Temperature	Composition (in mole %)			Equilibrium phases
		Na_2SiO_3	K_2SiO_3	$PbTiO_3$	
Ternary eutectic E_I	646°	35.0	33.0	32.0	Na_2SiO_3; $PbTiO_3$; $3K_2SiO_3 \cdot 2PbTiO_3$.
Ternary eutectic E_{II}	590	16.0	65.0	19.0	Na_2SiO_3; $3K_2SiO_3 \cdot 2PbTiO_3$; $3K_2SiO_3 \cdot Na_2SiO_3$.
Ternary transition P_{III}	620	14.0	66.0	20.0	K_2SiO_3; $3K_2SiO_3 \cdot 2PbTiO_3$; $3K_2SiO_3 \cdot Na_2SiO_3$.
Binary eutectic m		33.5	40.5	26.0	$3K_2SiO_3 \cdot 2PbTiO_3$; Na_2SiO_3.

An investigation of the system K_2SiO_3–Na_2SiO_3–$PbTiO_3$ showed that it is unsuitable for growing monocrystals of lead titanate. On complete solidification of the melts, together with crystals of $PbTiO_3$, crystals of $3K_2SiO_3 \cdot 2PbTiO_3$ precipitate, from which it is extremely difficult to separate the lead titanate.

We grew lead titanate monocrystals from a Na_2SiO_3 melt.

SUMMARY

1. The system K_2SiO_3–Na_2SiO_3–$PbTiO_3$ was investigated by the visual-polythermal method of fusibility, and it was found to be a stable profile of the prism Na, K, Pb || SiO_3, TiO_3.

2. In the system K_2SiO_3–$PbTiO_3$ a compound of composition $3K_2SiO_3 \cdot 2PbTiO_3$, which melted without decomposition, was established.

3. In the system K_2SiO_3–Na_2SiO_3, unlike the literature data, two compounds close in composition to $3K_2SiO_3 \cdot Na_2SiO_3$ and $3K_2SiO_3 \cdot 2Na_2SiO_3$, were established, which melted without decomposition.

4. In the profile K_2SiO_3–Na_2SiO_3–$PbTiO_3$ six regions of crystallization, three ternary and one binary nonvariant point, and one binary slope point were developed.

5. The system K_2SiO_3–Na_2SiO_3–$PbTiO_3$ cannot be recommended for the growing of lead titanate monocrystals. For this purpose it is better to use a sodium silicate melt.

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* T.p. = C.B. Translation pagination.

SODIUM ORTHONIOBATE

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Sodium orthoniobate is formed by the fusion of niobium pentoxide with soda, as was shown by one of us, together with Vikt. I. Spitsyn [1]. At that time we were unable to remove the excess of unreacted soda, and as a consequence of this we employed indirect proofs of the formation of sodium orthoniobate.

In the present work we set ourselves the goal of isolating the orthoniobate from the soda melt.

EXPERIMENTAL

Starting materials and methods of analysis. The niobium pentoxide which was used in the present investigation was obtained from a mixture of niobium and tantalum pentoxides, which had considerable impurities of the oxides of silicon, iron, tin, and traces of titanium.

The purification and separation of the niobium and tantalum pentoxides were effected just as we had done repeatedly [2,3]. The resulting niobium pentoxide was of a pure white color; an analysis showed a content of 99.40% Nb_2O_5, the rest was in an admixture, for which the tannin test for tantalum gave a negative result, i.e., the quantity of Ta_2O_5 was less than 0.5-0.2% which was in agreement with the sensitivity of the present method [4]. According to analysis the initial chemically pure sodium carbonate contained 99.58% Na_2CO_3 and 0.38% H_2O. The preparation was freed from an impurity of chlorine-ion.

The analysis of the substance obtained by the fusion of soda with niobium pentoxide, after extraction of the free soda, was carried out as follows: a weighed portion of the substance was dissolved in water, and a small quantity of 1 N sulfuric acid, in the presence of an indicator (methyl red), was added to the resulting solution, and immediately a flocculent precipitate of niobium pentoxide hydrate formed. In order to prevent the peptizing action of the mineral acid, a 0.05 N solution of ammonium hydroxide was carefully added dropwise until there was a neutral reaction. For a more complete coagulation of the precipitate the beaker and its contents was placed on a water bath. After transfer of the precipitate to the filter, and washing with a 5% solution of ammonium nitrate it was dried in an oven at 100°, and after ashing, it was calcined to a constant weight. The weight of the residue yielded the quantity of niobium pentoxide.

The filtrate, which contained sodium sulfate and ammonium nitrate, was evaporated to dryness on the water bath, and after careful heating was calcined to constant weight. The weight of the residue yielded the quantity of sodium sulfate.

Investigation of the Solubility of Soda in Organic Solvents

In the literature there were no data on the solubility of soda in organic solvents. We tested the following solvents and their mixtures: ethylene glycol, methyl alcohol, dioxane, glycerol and pyridine.

A weighed quantity of the anhydrous salt was treated with the solvent, and the bottle was closed with a stopper and placed in a "shaker". The shaking was continued for three days. After settling, the solvent was decanted, and the residue of the soda which did not dissolve was dried and weighed. The quantity of soda which dissolved was found by difference. For the heavy and difficultly-volatile solvents (glycerol, glycol) the solubility found was sharply reduced, because of the incomplete removal of the solvent from the residue of undissolved soda. The results of the investigation are recorded in the Table. From the data obtained it is evident that the best solvent for soda was ethylene glycol, and the next best was a ternary mixture consisting of glycol, methyl alcohol and glycerol; soda was practically insoluble in dioxane and pyridine.

As the investigations showed, the niobium pentoxide did not dissolve in organic solvents. The same thing was observed also for the action of organic solvents on the niobates [5].

Determination of the Solubility of Soda in Organic Solvents (Volume of Solvent 3 ml)

Solvent	Quantity of soda (in g) used	Volume ratio of solvents in mixture	Quantity (in g)		Solubility of soda (g/100 ml)
			Undissolved soda	Dissolved soda	
E.	0.25	-	0.18	0.07	2.3
E. + M.A.	0.23	1 : 1	0.20	0.03	1.0
M. A.	0.24	-	0.22	0.02	0.7
E. + D.	0.215	1 : 1	0.20	0.015	0.5
G. + M. A.	0.23	1 : 2	0.20	0.03	1.0
D. + M. A.	0.245	1 : 1	0.24	0.005	0.1
P. + M. A.	0.20	1 : 1	0.20	-	did not dissolve
M.A. + E. + G.	0.21	1 : 1 : 1	0.165	0.045	1.35
E. + G.	0.20	2 : 1	0.16	0.4	1.3
D.	0.24	-	0.24	-	did not dissolve
P.	0.23	-	0.23	-	did not dissolve

Note. G. – glycerol, E. – ethylene glycol, M.A. – methyl alcohol, P – pyridine, D – dioxane.

Isolation of Sodium Orthoniobate from the Soda Melt

A mixture of soda with niobium pentoxide, taken in a molar ratio of 9:1, i.e., with an evident excess of soda, after careful mixing was transferred to a platinum crucible and fused in a crucible furnace at a temperature of about 900°. The liquid melt was poured onto a silver plate, and after cooling, the fusion was pulverized in a jasper mortar and leached by long shaking with ethylene glycol. The leaching operation with ethylene glycol was repeated several times. The residual solvent was removed by washing the solid residue with methyl alcohol. The leached fusion was analyzed for its content of niobium pentoxide and sodium oxide, determined as the sulfate.

Found %: Nb_2O_5, 58.75, 57.81; Na_2O 41.72, 42.31. Na_3NbO_4. Calculated %: Nb_2O_5 58.91; Na_2O 41.09.

Thus, on the basis of the chemical analysis it may be concluded that, after removal of the excess soda, we obtained sodium orthoniobate. The somewhat elevated sodium oxide content may be explained by the incomplete removal of the excess soda by extraction with ethylene glycol.

SUMMARY

1. A non-aqueous solvent for sodium carbonate was found.

2. Sodium orthoniobate was isolated from the carbonate fusion by means of ethylene glycol.

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INVESTIGATION OF THE SYSTEM $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–ACETONE BY METHODS OF PHYSICO-CHEMICAL ANALYSIS

M. S. Barvinok

The system specified, consisting of two hetero-ionic salts and a solvent, in which a double decomposition reaction is possible, belongs to the quaternary reciprocal systems. The geometrical representation of equilibria in this system may be presented by a true pyramid with a square base, in the corners of which are situated the salts $Co(ClO_4)_2$, $CoCl_2$, Li_2Cl_2, $(LiClO_4)_2$, and with a summit, at which is located the solvent. The quantity of water in this system is determined by its content in the cobalt perchlorate crystal hydrate [1].

The possible combinations of salts participating in the reactions of this system consist of the following:

$Co(ClO_4)_2$–Li_2Cl_2
$CoCl_2$–$(LiClO_4)_2$
} Diagonal systems, corresponding to diagonals of the square.

$CoCl_2$–Li_2Cl_2
$CoCl_2$–$Co(ClO_4)_2$
$LiClO_4$–$LiCl$
$Co(ClO_4)_2$–$(LiClO_4)_2$
} Secondary systems, corresponding to the sides of the square.

In the present report the results of an investigation of sections of the following systems are cited: $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–CH_3COCH_3 [total salts 0.12 mole %, (H_2O 0.72 mole %), CH_3COCH_3 99.16 mole %], and $CoCl_2$–Li_2Cl_2–(H_2O)–CH_3COCH_3 [total salts 0.12 mole %, (H_2O 0.72 mole %), CH_3COCH_3 99.16 mole %], in which we observed a reaction between the salts.

We studied the light absorption, electrical conductivity, density and viscosity of the solutions as properties of the system investigated. We used the densities of the solutions for the calculation of their viscosity values.

Preparation of the substances and solutions. Methods of investigation. Cobalt perchlorate $Co(ClO_4)_2 \cdot 6H_2O$ was prepared from cobalt carbonate (analytical grade purity) and perchloric acid (of special purity) as we described earlier [1]. The cobaltous chloride $CoCl_2 \cdot 6H_2O$ was recrystallized twice before preparation of the solutions. The anhydrous cobaltous chloride was obtained by heating $CoCl_2 \cdot 6H_2O$ in a current of HCl at 250° [2]. Lithium chloride $LiCl \cdot H_2O$ (chemically pure) was recrystallized and dried at 80° [8] before preparation of the solutions.

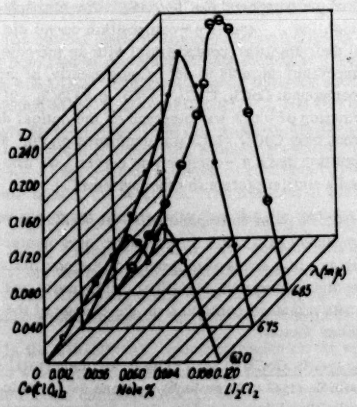

Fig. 1. Optical density of the system $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–CH_3COCH_3. Total salts 0.12 mole %(H_2O 0.72 mole %), CH_3COCH_3 99.16 mole % Layer depth 1 mm.

The acetone (analytical grade purity) was dried by calcium chloride and distilled twice. Tests of it were made as described in the literature [4]. The quantity of solvent required for preparation of the solution was calculated by volume, proceeding from its density at room temperature. The solutions were always freshly prepared. The concentration of the solutions was expressed in molar percentages.

We made measurements of the light absorption, electrical conductivity, viscosity and density of the solutions, as described earlier [1].

The optical density–composition isotherms at wavelengths where the specific points appeared most clearly are presented in the present work.

The system $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–acetone [total salts 0.12 mole %(H_2O 0.72 mole %), acetone 99.16 mole %].

At the concentration used, the cobalt perchlorate solutions had a pale-rose color, and at the layer depth of 1 mm, which was used in our measurements, did not absorb in the spectrum region studied. The lithium chloride solution also

did not absorb in the spectrum region in which the complex cobaltochloride compounds absorbed. In the spectrum region studied, only the cobaltochloride compounds which formed in the system absorbed.

In Fig. 1 the optical density isotherms are presented at wavelengths of 620, 675 and 685 mμ, plotted from the data of our measurements.

At a wavelength of 675 mμ the optical density–composition curve consisted of two branches intersecting at an acute angle at the maximum, the abscissa of which corresponds to a 2:3 ratio between $Co(ClO_4)_2$ and Li_2Cl_2, which corresponds to the compound $CoCl_2 \cdot LiCl$.

The formation of this compound in the system may be represented by the equation $2Co(ClO_4)_2 + 3Li_2Cl_2 = 2(CoCl_2 \cdot LiCl) + 4LiClO_4$. The abscissa of the maximum, corresponding to $CoCl_2 \cdot LiCl$, was not shifted in the 670-680 mμ spectrum region. On the optical density isotherm at 620 mμ two maxima were observed. The abscissa of one of them corresponded to a 1:1 ratio between $Co(ClO_4)_2$ and Li_2Cl_2. In this case the formation of the compound may be expressed by the equation $Co(ClO_4)_2 + Li_2Cl_2 = CoCl_2 + 2LiClO_4$. The second maximum on the optical density isotherm at a wavelength of 620 mμ, indicated the presence of complex cobaltochloride compounds, together with $CoCl_2$, in the system. The light absorption of the complex cobaltochloride compounds increased and became predominant with an increase of the wavelength; therefore, on the optical density isotherm at a wavelength of 675 mμ one maximum corresponding to the formation of a complex cobaltochloride compound in the system was observed. In the spectrum region of 685 mμ the abscissa of the maximum was shifted toward an increase of lithium chloride. At a wavelength of 685 mμ on the optical density–composition curve a maximum was observed, the abscissa of which corresponded to a 1:2 ratio between $Co(ClO_4)_2$ and Li_2Cl_2, which indicated the formation of the compound $CoCl_2 \cdot 2LiCl$ in the solution.

Thus, in the system $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–acetone with total salts of 0.12 mole %, the formation of cobaltochloride compounds of different degrees of complexity was observed on the optical density isotherms in different spectrum regions.

In order to detect whether the compounds the formation of which found expression on the optical density isotherms were observed on the isotherms of the other properties of the system $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–acetone, we investigated its electrical conductivity, viscosity and density.

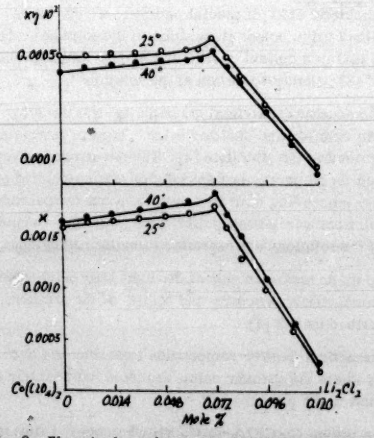

Fig. 2. Electrical conductivity, and electrical conductivity corrected for the viscosity of the system $Co(ClO_4)_2$–Li_2Cl_2–(H_2O)–CH_3COCH_3. Total salts 0.12 mole (H_2O 0.72 mole%), CH_3COCH_3 99.16 mole %.

In Fig. 3 are presented the κ–composition and $\kappa\eta$–composition curves at 25 and 40° plotted from the data of our measurements.

Each of the κ–composition and $\kappa\eta$–composition curves consists of two branches which intersect at a maximum, the abscissa of which corresponds to a 2:3 ratio between $Co(ClO_4)_2$ and Li_2Cl_2, which indicates the formation in the system of the compound $CoCl_2 \cdot LiCl$. The maxima on the κ-composition and $\kappa\eta$–composition curves did not change their abscissas (composition) with an increase of the temperature from 25 to 40°. Consequently, of the three compounds $CoCl_2$, $CoCl_2 \cdot LiCl$, and $CoCl_2 \cdot 2LiCl$ the formation of which was observed on the optical density isotherms, only $CoCl_2 \cdot LiCl$ was confirmed on the κ–composition and $\kappa\eta$–composition curves. We also observed a similar picture in other systems [1].

A specific point corresponding to the formation of the compound $CoCl_2 \cdot LiCl$ in the system was observed on the diagrams of a series of properties of the equilibrium system: light absorption, electrical conductivity and $\kappa\eta$. Its abscissa remained constant with the change of the equilibrium factors.

The system $CoCl_2$–Li_2Cl_2–(H_2O)–acetone [total salts 0.12 mole %, (H_2O 0.72 mole %), acetone 99.16 mole %]. Independently of their concentration, the acetone solutions of cobaltous chloride were of a blue color. In the 600-700

m μ spectrum region the absorption curve of an acetone solution of cobaltous chloride [5] had a flat maximum similar to that which was observed for cobaltous chloride in a concentrated aqueous solution of HCl [6]. The addition of lithium chloride to an acetone solution of cobaltous chloride was accompanied by a small rise of the absorption curve and by a small shift of it into the long-wave region of the spectrum [5]. The similarity of the absorption curve of an acetone solution of cobaltous chloride to that of $CoCl_2$ in a concentrated aqueous solution of HCl indicated the presence in the acetone solution of complex cobaltochloride compounds, which was also confirmed by Dirking's experiments [7] in the study of the migration of ions under the influence of an electric current.

The migration of cobalt to the anode, observed during the passage of an electric current through the solution is possible only when the cobalt ion enters into the composition of the complex cobaltochloride ions. Since in acetone solutions of cobaltous chloride, under the influence of an electric current, a simultaneous transfer of cobalt to the cathode is also observed, then in them there are bivalent cobalt cations, together with the complex cobaltochloride anions. The presence of the bivalent cobalt cations was confirmed by a study of the light absorption of an acetone solution of cobaltous chloride, which showed that absorption characteristic of cobalt cations [7] is observed in this solution in the 500-520 m μ spectrum region.

For an aqueous solution of $CoCl_2$ with a very large excess of HCl, in which practically all of the cobalt ions are found to be in the composition of the complex cobaltochloride formations, no light absorption in this spectrum region was observed [6]. Together with cobalt ions, complex cobaltochloride compounds and cobaltochloride anions, undissociated $CoCl_2$ molecules are included in acetone solutions of cobaltous chloride.

Besides the salts and acetone, as was indicated above, a small quantity of water was included in solutions of the system studied. The effect of water on the light absorption of acetone solutions of cobaltous chloride was described in the literature [5], from which it is evident that the absorption curve of a water-acetone solution containing 2 wt. % water in the 600-670 m μ region, in which the complex cobaltochloride formation absorbs, runs together with the curve corresponding to the light absorption of an anhydrous acetone solution of cobaltous chloride. The first curve is somewhat reduced in the 675 m μ spectrum region, i.e., a small decrease of the light absorption was observed. In solutions of the system which we studied, the quantity of water was equal to 0.2% by wt., i.e., it was smaller by a factor of 10 than in the water-acetone solution indicated above. It can be assumed that such a small quantity of water shows no appreciable influence on their light absorption.

However, it does not follow from this that on introduction of water into acetone solutions of cobaltous chloride no new compounds are formed, since the latter might have an absorption even in the spectrum region where the above-considered absorption curves run together, but without expressed maxima. For examination of the problem of the effect of water added with the crystal hydrates to acetone solutions of our system, it was necessary to study the system $CoCl_2-Li_2Cl_2-CH_3COCH_3$ and to compare the results obtained with the data of the investigation of the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$.

The reaction of cobaltous chloride and lithium chloride in the latter system was clearly observed on the optical density–composition, κ–composition and $\kappa\eta$–composition isotherms.

The optical density–composition isotherms for wavelengths of 680 and 705 m μ are presented in Fig. 3. They consisted of two branches intersecting at a maximum, the abscissa of which corresponds to a 2:1 ratio between $CoCl_2$ and Li_2Cl_2. The specific point observed on the optical density isotherms, corresponding to the formation in the system of the compound $CoCl_2 \cdot LiCl_2$ was also confirmed on the κ–composition and $\kappa\eta$–composition isotherms, as was evident from Fig. 4, where the acetone solutions of cobaltous chloride and lithium chloride show a small electrical conductivity, which is practically unchanged in the range from 25 to 40°. The low electrical conductivity of the acetone solutions of cobaltous chloride and lithium chloride indicated the low degree of dissociation of these salts in the solutions. The mixtures of acetone solutions of cobaltous chloride and lithium chloride had a higher electrical conductivity than did the initial solutions.

The κ–composition and $\kappa\eta$–composition isotherms (Fig. 4) consisted of two branches intersecting at a maximum, the abscissa of which corresponded to a 2:1 ratio between $CoCl_2$ and Li_2Cl_2, which indicated the formation of the compound $CoCl_2 \cdot LiCl$ in the system. The abscissa of the maximum corresponding to this compound did not shift with a change of the temperature from 25 to 40°.

In the 610-630 m μ spectrum region on the optical density–composition isotherms the formation of a compound was observed, the abscissa of which corresponded to a 1:1 ratio between the $CoCl_2$ and Li_2Cl_2, which corresponded to the compound $CoCl_2 \cdot 2LiCl$.

If, on construction of the light absorption–composition diagram, the absorption of the original component is excluded (solutions of lithium chloride did not absorb in the part of the spectrum investigated), calculating the value of $\overline{D}$–the composition, as the difference of the optical densities of the solutions corresponding to the systems $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ and $CoCl_2-(LiClO_4)_2-(H_2O)-CH_3COCH_3$, total salts of 0.12 mole %, (H_2O 0.72 mole %), CH_3COCH_3 99.16 mole %[salt pair $CoCl_2-(Li ClO_4)_2$ in the quaternary reciprocal system formed a stable diagonal; acetone solutions of lithium perchlorate did not absorb in the region of the spectrum studied], then on the $\overline{D}$–composition isotherm at λ 690 mμ a maximum was observed, the abscissa of which corresponds to a 2:3 ratio between $CoCl_2$ and Li_2Cl_2, which corresponds to the compound $CoCl_2 \cdot 3LiCl$. However, the formation in the system of the complex cobaltochloride compounds $CoCl_2 \cdot 2LiCl$ and $CoCl_2 \cdot 3LiCl$ was not confirmed on the κ–composition and $\kappa\eta$–composition isotherms. This is accounted for by the fact that the light absorption, unlike the other properties, is a selective property, since each chemical individual has its corresponding absorption spectrum, and on study of the light absorption of a system including several chemical individuals, we can select the wavelength of light at which one of the chemical individuals chiefly absorbs. The light absorption of the remaining chemical individuals present in the system is equal to zero or is extremely insignificant compared with the light absorption of the chemical individual being studied.

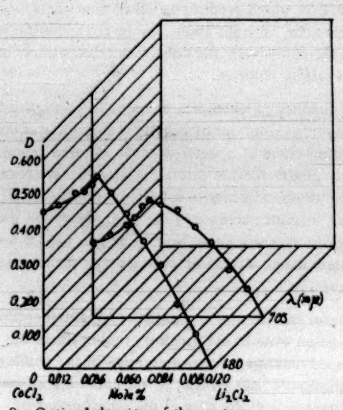

Fig. 3. Optical density of the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$. Total salts 0.12 mole %, (H_2O 0.72 mole %), CH_3COCH_3 99.16 mole %. Layer depth 1 mm.

The system $CoCl_2-Li_2Cl_2-CH_3COCH_3$ [total salts 0.12 mole %, acetone 99.88 mole %]. Since in the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ with total salts of 0.12 mole % the formation of the compound $CoCl_2 \cdot LiCl$ was confirmed by the presence of a specific point on the optical density–composition (Fig. 3), κ–composition and $\kappa\eta$–composition isotherms (Fig. 4), which in all these curves appear very clearly as an intersection of their branches at an acute maximum, it was interesting to follow the effect of the water added with the crystal hydrates on the composition of the compound which formed in the system. The study of this system presented difficulties, since the crystal hydrates of cobaltous chloride and lithium chloride were readily dehydrated.

In Fig. 5 the optical density–composition curves are presented for the wavelengths where the specific point is most distinct. The abscissa of this point corresponds to a 2:1 ratio between $CoCl_2$ and Li_2Cl_2, which corresponds to the formation of the compound $CoCl_2 \cdot LiCl$ in the system.

A comparison of the optical density–composition curves represented in Figs. 3 and 5 showed that the presence of water added with the crystal hydrates of the salt components in the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ did not shift the abscissa of the specific point which corresponded to the formation of the compound $CoCl_2 \cdot LiCl$ in the system, and did not give rise to a change of the nature of the maximum, at which branches of the optical density–composition isotherm intersected, where the specific point was especially clear. As is evident in Figs. 3 and 5, the presence of water in the system which we studied, is indicated only by the fact that the optical density–composition curves on which the specific point was most distinct for the systems $CoCl_2-Li_2Cl_2-CH_3COCH_3$ and $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ did not appear to be isochromes.

The small shift of the optical density–composition curves in the direction of an increase of wavelengths, which was observed for the optical density–composition diagrams represented in Figs. 3 and 5, with retention of the abscissa value (composition) of the specific point, may specify a change of the condition of the solvate film of the cobaltochloride compound $CoCl_2 \cdot LiCl$. The latter is connected with the appearance in the system of water molecules, which can influence both the composition of the solvate film, consisting of acetone molecules in a system containing no water, and the stability of the bond between the acetone molecules and the complex cobaltochloride compounds. The presence in the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ of water even in such a negligible quantity (0.72 mole % or 0.2 % by wt.) had an influence on the electrical conductivity of the cobaltous chloride and lithium chloride solutions. Values of the electrical conductivity of the solutions of the system $CoCl_2-Li_2Cl_2-CH_3COCH_3$ with total salts of 0.12 mole % were cited in Table 1. A comparison of these data with

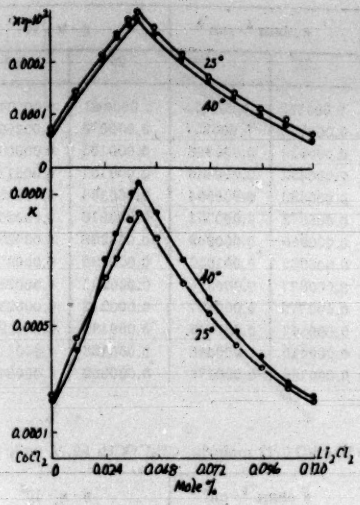

Fig. 4. Electrical conductivity and electrical conductivity corrected for viscosity of the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$. Total salts 0.12 mole %, (H_2O 0.72 mole %), CH_3COCH_3 99.16 mole %.

electrical conductivity data of solutions of $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ with total salts of 0.12 mole % (H_2O 0.72 mole %), and acetone 99.16 mole %, cited in Table 2, showed that the electrical conductivity of the cobaltous chloride solution with 0.72 mole % of water present in it increased at 25° by 16.3% and at 40° by 20%.

The increase of the electrolytic conductivity occurred chiefly due to the increase of dissociation of cobaltous chloride, since at the same time the viscosity decreased negligibly (by 2.6%).

A similar picture was observed for lithium chloride solutions. The electrical conductivity of lithium chloride solutions, under the influence of the water present, increased by 27% both at 25 and at 40°. At the same time the viscosity decreased negligibly (about 1%). The κ-composition and $\kappa\eta$-composition isotherms constructed from the data of Table 1, are presented in Fig. 6. They consist of two branches, which intersect at a point, the abscissa of which corresponds to a 2:1 ratio between $CoCl_2$ and Li_2Cl_2, which corresponds to the formation of the compound $CoCl_2 \cdot LiCl$ in the system. A comparison of Figs. 4 and 6, in which the κ-composition and $\kappa\eta$-composition isotherms are represented for solutions of the systems $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ and $CoCl_2-Li_2Cl_2-CH_3COCH_3$ showed that on the κ-composition and $\kappa\eta$-composition curves, not only the abscissa of the specific point which corresponded to the formation in the system of the compound $CoCl_2 \cdot LiCl$ remains constant, but also the character of the maximum at which the branches of the isotherms intersect remains constant.

Thus, in spite of the fact that the water present in the system appreciably affects the dissociation of cobaltous chloride and lithium chloride in the original solutions, the latter did not indicate the position of the specific point and the nature of the intersection of the branches of the optical density-composition and $\kappa\eta$-composition isotherms at the specific point.

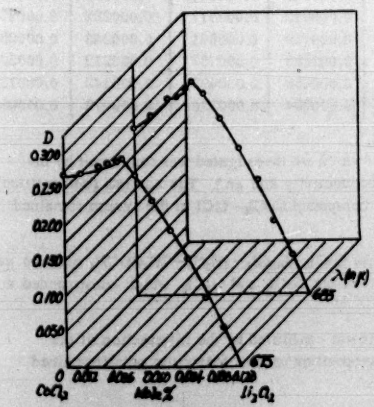

Fig. 5. Optical density of the system $CoCl_2-Li_2Cl_2-CH_3COCH_3$. Total salts 0.12 mole %, CH_3COCH_3 99.88 mole %. Layer depth 0.52 mm.

SUMMARY

1. The quadruple reciprocal system $Co(ClO_4)_2-Li_2Cl_2-CH_3COCH_3$ was investigated by the methods of physico-chemical analysis.

2. The light absorption, electrical conductivity, viscosity and density of the solutions were studied as properties of the system.

3. The light absorption and the electrical conductivity of the solutions were the properties most sensitive to the formation of complex cobaltochloride compounds in the system. The light absorption was not only the most sensitive property, but also the most selective.

4. On the optical density isotherms of the system $Co(ClO_4)_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$, with total salts of 0.12 mole %, the formation of the compounds $CoCl_2 \cdot LiCl$ and $CoCl_2 \cdot 2LiCl$ was observed. On the electrical conductivity isotherms the formation in the system of only the compound $CoCl_2 \cdot LiCl$ was observed.

TABLE 1

System $CoCl_2 - Li_2Cl_2 - CH_3COCH_3$ (Total salts 0.12 mole %, CH_3COCH_3 99.88 mole %)

Composition (mole %)		$d_4^{t°}$		$\eta \cdot 10^3$ centipoises		κ, $ohms^{-1} \cdot cm^{-1}$		$\eta \cdot \kappa \cdot 10^5$	
Li_2Cl_2	$CoCl_2$	25°	40°	25°	40°	25°	40°	25°	40°
0.120	-	0.78614	0.76885	0.3145	0.2733	0.000152	0.000155	0.000048	0.000042
0.108	0.012	0.78642	0.76858	0.3098	0.2686	0.000241	0.000257	0.000075	0.000069
0.096	0.024	0.78645	0.76927	0.3155	0.2704	0.000334	0.000366	0.000105	0.000099
0.084	0.036	0.78653	0.76917	0.3152	0.2698	0.000433	0.000480	0.000137	0.000129
0.072	0.048	0.78653	0.76916	0.3086	0.2658	0.000532	0.000594	0.000164	0.000158
0.060	0.060	0.78656	0.76929	0.3128	0.2663	0.000672	0.000751	0.000210	0.000200
0.048	0.072	0.78664	0.76927	0.3116	0.2690	0.000855	0.000949	0.000266	0.000255
0.040	0.080	0.78681	0.76954	0.3077	0.2662	0.000935	0.001039	0.000288	0.000277
0.036	0.084	0.78678	0.76958	0.3090	0.2640	0.000877	0.000974	0.000271	0.000257
0.030	0.090	0.78681	0.76954	0.3118	0.2691	0.000776	0.000857	0.000242	0.000231
0.024	0.096	0.78676	0.76939	0.3073	0.2664	0.000647	0.000716	0.000199	0.000191
0.012	0.108	0.78675	0.76950	0.3089	0.2659	0.000415	0.000446	0.000128	0.000118
-	0.120	0.78660	0.76928	0.3163	0.2749	0.000196	0.000176	0.000062	0.000048

TABLE 2

System $CoCl_2 - Li_2Cl_2 - (H_2O) - CH_3COCH_3$ (Total salts 0.12 mole %, (H_2O 0.72 mole %), CH_3COCH_3 99.16 mole %)

Composition (mole %)		$d_4^{t°}$		$\eta \cdot 10^3$ centipoises		κ $ohms^{-1} \cdot cm^{-1}$		$\eta \cdot \kappa \cdot 10^5$	
Li_2Cl_2	$CoCl_2$	25°	40°	25°	40°	25°	40°	25°	40°
0.120	-	0.78678	0.76956	0.3103	0.2702	0.000208	0.000212	0.000064	0.000057
0.108	0.012	0.78680	0.76961	0.3128	0.2702	0.000269	0.000285	0.000084	0.000077
0.096	0.024	0.78670	0.76950	0.3124	0.2702	0.000347	0.000382	0.000108	0.000103
0.084	0.036	0.78680	0.76951	0.3121	0.2690	0.000699	0.000481	0.000218	0.000129
0.072	0.048	0.78702	0.76969	0.3085	0.2699	0.000543	0.000606	0.000168	0.000164
0.060	0.060	0.78705	0.76968	0.3119	0.2692	0.000661	0.000740	0.000206	0.000199
0.048	0.072	0.78711	0.76976	0.3150	0.2749	0.000831	0.000925	0.000262	0.000254
0.040	0.080	0.78709	0.76995	0.3186	0.2750	0.000921	0.001024	0.000293	0.000282
0.036	0.084	0.78740	0.77009	0.3092	0.2707	0.000913	0.001017	0.000282	0.000275
0.030	0.090	0.78735	0.77052	0.3198	0.2763	0.000759	0.000841	0.000243	0.000232
0.024	0.096	0.78741	0.77009	0.3104	0.2680	0.000683	0.000757	0.000212	0.000203
0.012	0.108	0.78736	0.76993	0.3097	0.2684	0.000458	0.000492	0.000142	0.000132
-	0.120	0.78729	0.77000	0.3083	0.2658	0.000234	0.000220	0.000072	0.000059

5. The formation of the compound $CoCl_2 \cdot LiCl$ in the system which we investigated was confirmed by the isotherms of a number of properties (optical density, electrical conductivity and $\kappa\eta$). The abscissa (composition) of the specific point which corresponded to the formation of the compound $CoCl_2 \cdot LiCl$ in the system remained constant with a change of the equilibrium factors (temperature).

6. On the optical density–composition isotherms of the system $CoCl_2 - Li_2Cl_2 - (H_2O) - CH_3COCH_3$ maxima were observed, the abscissas of which corresponded to a 2:1 ratio between the $CoCl_2$ and Li_2Cl_2, which corresponded to the formation of the compound $CoCl_2 \cdot LiCl$.

The abscissa of the maximum on the optical density isotherms was confirmed by the intersection of the κ–composition and $\kappa\eta$ – composition branches. The abscissa (composition) of this maximum point remained constant with a change of temperature from 25 to 40°.

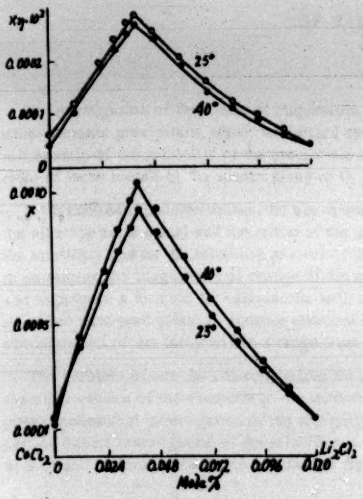

Fig. 6. Electrical conductivity, and electrical conductivity corrected for viscosity, of the system $CoCl_2-Li_2Cl_2-CH_3COCH_3$.
Total salts 0.12 mole %, CH_3COCH_3 99.18 mole %.

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7. On the optical density–composition and electrical conductivity–composition isotherms of the system $CoCl_2-Li_2Cl_2-CH_3COCH_3$ with total salts of 0.12 mole %, maxima were also observed, the abscissas of which corresponded to a 2:1 ratio between the $CoCl_2$ and Li_2Cl_2. Thus, the presence of water, added with the crystal hydrates, in the system $CoCl_2-Li_2Cl_2-(H_2O)-CH_3COCH_3$ gave rise to no change of the composition abscissa of the specific point on the density, electrical conductivity and $\kappa\eta$-isotherms.

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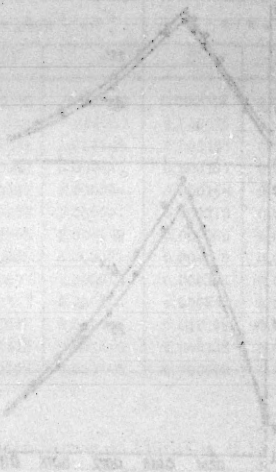

SOLUBILITY OF SILVER BROMATE IN AQUEOUS SOLUTIONS OF ZINC AND CADMIUM NITRATES

Yu. L. Lelchuk

An investigation of the effect of magnesium, calcium, strontium and barium nitrates on the solubility of the silver bromate precipitate, which we carried out earlier, enabled us to draw definite conclusions concerning the relationship of the solubility of the precipitate to the concentration of the corresponding electrolyte and to the order of these metals in the second group of D. I. Mendeleev's periodic system [1].

With sufficient conclusiveness, the above-mentioned investigation showed that the larger the atomic weight of the alkaline earth metal and the radius of the cation of the external electrolyte, the greater the influence on the solubility and on the solubility product of the precipitate. The experimental data on these systems enabled us to determine the magnitudes of change of the solubility of silver bromate at different concentrations of electrolytes, and to propose a formula for calculation, with an accuracy sufficient for practical purposes, of the solubility of the silver bromate precipitate in aqueous solutions of magnesium, calcium, strontium and barium nitrates, at any concentration of the latter within a range from 0.001 to 1 M.

The problem of how far our conclusions for magnesium, calcium, strontium and barium nitrates are correct for the other cations of the elements of the second group of the periodic system may be solved only by an additional physico-chemical investigation of the solubility in the appropriate ternary systems. In connection with this we carried out an investigation of the solubility in the systems $AgBrO_3-Zn(NO_3)_2-H_2O$ and $AgBrO_3-Cd(NO_3)_2-H_2O$ at zinc and cadmium nitrate concentrations from 0.001 to 1 M.

EXPERIMENTAL

The production of chemically pure silver bromate and the method of investigation were described earlier [1,2].

Aqueous solutions of zinc and cadmium nitrates were obtained by suitable dilution of 1 M solutions of chemically pure $Zn(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ by double-distilled water.

Experiments on the solubility determination in these systems were carried out in 400-500 ml brown glass bottles in a water thermostat at 25 $\pm 1^\circ$. The silver bromate concentration was determined gravimetrically as silver chloride [3].

In the tables below such symbols as the following are cited: μ – the ionic strength of the solution, γ – the activity coefficient, L_p – the solubility product of the precipitate, L_a – the activity product, $\underline{a}$ – the coefficient in the Debye and Hückel formula for calculation of the activity coefficient of the precipitate at concentrations of external electrolytes exceeding those of the Debye region [4].

System $AgBrO_3-Zn(NO_3)_2-H_2O$ (Table 1). As is evident from the data of Table 1, the solubility of the silver bromate precipitate increased steadily with an increase of the zinc nitrate concentration. In a 1 M solution of zinc nitrate the silver bromate solubility became equal to $1.93 \cdot 10^{-2}$, which is 2.34 times larger than that of the precipitate in water.

The activity coefficient and the solubility product of the silver bromate changed in accordance with this. With an increase of the concentration of the external electrolyte in this system, the activity coefficient of $AgBrO_3$ changed from 0.890 for a 0.001 M solution of zinc nitrate to 0.384 for a 1 M solution, i.e., it decreased by a factor of 2.32. The solubility product of the precipitate in the ternary system considered, as also in all the systems which we studied earlier [1,2,5], changed considerably with a change of the concentration of the external electrolyte. In a 0.001 M solution of zinc nitrate, the value of the solubility product is close to its value in pure water; in a 1 M solution of $Zn(NO_3)_2$ it amounts to about $3.72 \cdot 10^{-4}$, i.e., it increases 5.47 times.

An analysis of all the experimental data and the results of the corresponding calculations which we obtained for this system, and a comparison of these data with those which we obtained earlier in the study of the behavior of the silver bromate precipitate in solutions of magnesium, calcium, strontium and barium nitrates, indicated that the effect of the zinc nitrate on the most important properties of the silver bromate precipitate in the system

TABLE 1

Solubility of $AgBrO_3$ in the System $AgBrO_3-Zn(NO_3)_2-H_2O$

Concentration (M)					
$Zn(NO_3)_2$	$AgBrO_3$	μ	γ	L_p	$L_a \cdot 10^5$
0.000	$8.25 \cdot 10^{-3}$	0.0082	0.900	$6.80 \cdot 10^{-5}$	5.50
0.001	$8.43 \cdot 10^{-3}$	0.0114	0.890	$7.11 \cdot 10^{-5}$	5.63
0.003	$8.75 \cdot 10^{-3}$	0.0177	0.867	$7.65 \cdot 10^{-5}$	5.75
0.010	$9.12 \cdot 10^{-3}$	0.0391	0.815	$8.32 \cdot 10^{-5}$	5.52
0.030	$1.02 \cdot 10^{-2}$	0.1002	0.737	$1.04 \cdot 10^{-4}$	5.64
0.100	$1.16 \cdot 10^{-2}$	0.3120	0.619	$1.34 \cdot 10^{-4}$	5.13
0.300	$1.47 \cdot 10^{-2}$	0.9150	0.502	$2.16 \cdot 10^{-4}$	5.44
1.000	$1.93 \cdot 10^{-2}$	3.0190	0.384	$3.72 \cdot 10^{-4}$	5.50

Note. The value of the coefficient a in the Debye and Hückel formula was equal to 1.936.

TABLE 2

Solubility of $AgBrO_3$ in the System $AgBrO_3-Cd(NO_3)_2-H_2O$

Concentration (M)						
$Cd(NO_3)_2$	$AgBrO_3$	μ	γ	L_p	$L_a \cdot 10^5$	a
0.000	$8.25 \cdot 10^{-3}$	0.0082	0.900	$6.80 \cdot 10^{-5}$	5.50	
0.001	$8.13 \cdot 10^{-3}$	0.0111	0.892	$6.61 \cdot 10^{-5}$	5.26	
0.003	$8.42 \cdot 10^{-3}$	0.0174	0.870	$7.09 \cdot 10^{-5}$	5.37	
0.010	$8.75 \cdot 10^{-3}$	0.0388	0.820	$7.66 \cdot 10^{-5}$	5.16	
0.030	$9.10 \cdot 10^{-3}$	0.0991	0.746	$8.28 \cdot 10^{-5}$	4.60	2.385
0.100	$1.04 \cdot 10^{-2}$	0.3100	0.637	$1.08 \cdot 10^{-4}$	4.38	
0.300	$1.32 \cdot 10^{-2}$	0.9130	0.530	$1.74 \cdot 10^{-4}$	4.89	
1.000	$1.74 \cdot 10^{-2}$	3.0170	0.426	$3.03 \cdot 10^{-4}$	5.50	

$AgBrO_3-Zn(NO_3)_2-H_2O$ was approximately the same as corresponding concentrations of strontium nitrate showed in the system $AgBrO_3-Sr(NO_3)_2-H_2O$.

In the entire concentration range of zinc and strontium nitrates which we studied, the activity coefficients of $AgBrO_3$ were approximately identical (Table 4). In Table 3 composite data are presented, characterizing the behavior of the precipitate in 1 M solutions of zinc, cadmium, magnesium, calcium and strontium nitrates. As is evident from these data, the zinc cation has approximately the same effect on the behavior of the precipitate as had the strontium cation. In connection with this all the conclusions which we drew earlier relative to the system $AgBrO_3-Sr(NO_3)_2-H_2O$, are also essentially correct for the ternary system $AgBrO_3-Zn(NO_3)_2-H_2O$.

The system $AgBrO_3-Cd(NO_3)_2-H_2O$ (Table 2). The solubility of silver bromate in the ternary system considered increased steadily with an increase of the concentration of the external electrolyte. This fact, above all, indicated the absence in this system of any clear chemical reaction between the cadmium nitrate and the silver bromate.

In all the ternary systems which we studied earlier, where the nitrates of metals of the main sub-groups of the corresponding groups of elements of the periodic system [1,2] were used as the electrolytes, the cations with the largest ionic radii and atomic weights provided the largest increase of the solubility and solubility product of the precipitate, which however, did not occur in systems of silver bromate–zinc nitrate–water, and silver bromate–cadmium nitrate–water. As is evident from the data of Tables 1-3, the zinc cation influences the behavior of the silver bromate precipitate to a considerably greater extent than does the cadmium cation.

On comparison of the ternary system $AgBrO_3-Cd(NO_3)_2-H_2O$ with that studied earlier, it should especially be noted that in all the most important properties characterizing the effect of the cadmium ion concentration on the behavior of the silver bromate precipitate, the system considered was very close to the system $AgBrO_3-Mg(NO_3)_2-H_2O$ [1].

TABLE 3

Behavior of $AgBrO_3$ in Molar Solutions of $Me(NO_3)_2$

Electrolyte	$C_{AgBrO_3} \cdot 10^3$	$L_p' : L_p$	$L_i' : L_i$	a
$Zn(NO_3)_2$	1.93	5.47	2.34	1.94
$Cd(NO_3)_2$	1.74	4.45	2.11	2.39
$Mg(NO_3)_2$	1.73	4.41	2.10	2.41
$Ca(NO_3)_2$	1.81	4.80	2.19	2.19
$Sr(NO_3)_2$	1.94	5.50	2.35	1.91

Note. L_p' and L_p are the solubility products $AgBrO_3$ in a 1 M solution of the nitrate and in water, respectively; L_i' and L_i are the solubility of $AgBrO_3$ in a 1 M solution of the nitrate and in water, respectively.

TABLE 4

Activity Coefficients of $AgBrO_3$ in Aqueous Solutions of Nitrates of the Metals of the Second Group of the Periodic System

$Me(NO_3)_2$ (M)	γ_{AgBrO_3} in solutions						Average value of γ_{AgBrO_3}
	$Zn(NO_3)_2$	$Cd(NO_3)_2$	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$Sr(NO_3)_2$	$Ba(NO_3)_2$	
0.001	0.890	0.892	0.891	0.893	0.890	0.891	0.891
0.003	0.867	0.870	0.870	0.870	0.867	0.868	0.869
0.010	0.815	0.820	0.820	0.818	0.815	0.816	0.817
0.030	0.737	0.746	0.746	0.741	0.736	0.736	0.740
0.100	0.619	0.637	0.634	0.630	0.619	0.619	0.626
0.300	0.502	0.530	0.532	0.519	0.500	0.498	0.513
1.000	0.384	0.426	0.428	0.410	0.382	-	0.406

In the ternary system $AgBrO_3-Cd(NO_3)_2-H_2O$ the cadmium cation showed practically the same effect on the activity coefficient, solubility and solubility product of the precipitate as did the magnesium cation in the system $AgBrO_3-Mg(NO_3)_2-H_2O$ (Tables 3,4). It is known [6] that cadmium nitrate is very close to magnesium nitrate in certain other properties also. Thus, for example, the equivalent electrical conductivity of a 0.01 N solution of magnesium nitrate at 18° was equal to 94.7, and of cadmium nitrate, 96.0 Ω^{-1} cm^2/ g-equiv. The equivalent electrical conductivity of 0.1 N solutions of magnesium and cadmium nitrates was 80.5 and 80.8 Ω^{-1} cm^2/ g-equiv, respectively. Under different conditions the equivalent electrical conductivity of the nitrates of all the other metals of the second group of the periodic system differ appreciably from these values.

It was shown earlier [1] that the calculation of the solubility of silver bromate in aqueous solutions of the alkaline earth metal nitrates in a concentration range from 0.001 to 1 M at 25° may, with an accuracy sufficient for practical purposes, be made by the formula:

$$C_{AgBrO_3} = \sqrt{\frac{L_a}{\gamma^2}},$$

where L_a is the activity product of $AgBrO_3$, which we found to be $5.50 \cdot 10^{-5}$; γ is the average activity coefficient of $AgBrO_3$ in aqueous solutions of magnesium, calcium, strontium and barium nitrates (determined from the curve of the relation of the average activity coefficient to the concentration of the external electrolyte).

The average activity coefficients of silver bromate (Table 4) hardly changed, if in their determination we also consider the behavior of the precipitate in aqueous solutions of zinc and cadmium nitrates. This fact gives us a rule for extending the above-mentioned recommendation to aqueous solutions of zinc and cadmium nitrates at concentrations of the latter from 0.001 to 1 M.

SUMMARY

1. The solubility of the silver bromate precipitate in aqueous solutions of zinc and cadmium nitrates, at external electrolyte concentrations from 0.001 to 1 M at 25°, was investigated.

2. It was found that the solubility and solubility product of the $AgBrO_3$ precipitate in these systems increased steadily with an increase of the external electrolyte concentration.

3. The experimental data of these systems were applied to the determination of the activity coefficients of the silver bromate in aqueous solutions of zinc and cadmium nitrates.

4. The magnitudes of the change of the solubility product of the silver bromate precipitate in aqueous solutions of zinc and cadmium nitrates in relation to the ionic strengths of the solutions were shown.

5. It was demonstrated that zinc nitrate has approximately the same effect on the behavior of the $AgBrO_3$ precipitate as does strontium nitrate in the system $AgBrO_3-Sr(NO_3)_2-H_2O$, but that cadmium nitrate has approximately the same effect as magnesium nitrate in the system $AgBrO_3-Mg(NO_3)_2-H_2O$.

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VISUAL – POLYTHERMAL INVESTIGATION OF THE SOLUBILITY OF SALTS IN A RECIPROCAL SYSTEM OF NITRATES AND CHLORIDES OF BARIUM AND CALCIUM AT 80, 100, 120°

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The solubility of salts in a reciprocal system of the chlorides and nitrates of barium and calcium is presented in the literature only in the form of fragmental, disconnected data, and chiefly at relatively low temperatures [1-4]. This system has also been little studied by fusibility [5-7].

The results which we cited of a study of the mutual solubility of salts in the system $Ba^{\cdot\cdot}, Ca^{\cdot\cdot} \| Cl', NO_3'$, in the presence of water at 80, 100 and 120°, are part of our investigation of the solubility of the salts at elevated temperatures in reciprocal systems of the chlorides and nitrates of alkali and alkaline earth metals.

The purpose of the investigation was the study of the solubility of the salts, on the one hand, and the role of water, on the other, in a temperature range where water from the solvent is converted gradually to the state of the dissolved component, in the system, and where the effect of the polar water molecules on the solubility of the salt components decreases.

EXPERIMENTAL

The study of the solubility at 80, 100 and 120° was carried out by the visual-polythermal method by E. I. Akhumov and B. B. Vasilyev's method [4] in upright, sealed glass tubes.

The following systems and internal profiles were studied: 1) systems representing secondary sides of the projection of the solubility of the reciprocal system onto a square: $Ba(NO_3)_2$ $BaCl_2-H_2O$, $Ba(NO_3)_2-Ca(NO_3)_2-H_2O$, $CaCl_2-BaCl_2-H_2O$; 2) the system $Ba(NO_3)_2-CaCl_2-H_2O$ (diagonal profile); 3) internal profile representing the system $\{[9.5$ mole% $Ba(NO_3)_2 + 90.5$ mole% $Ca(NO_3)_2] + CaCl_2\} \rightarrow H_2O$.

The results of the experiments were represented as isotherms of 80, 100 and 120°, obtained after treatment of the visual-polythermal data by selection from them of the isothermals and conversion of the latter to mole percentages of salts in the dry residue, and conversion of the characteristic water contents as the number of molecules occurring for 100 molecules of salts of the dry residue (Tables 1-7; Figs. 1-8).

Chemical reaction was absent in both systems. The $Ba(NO_3)_2$ saturation curve (Fig.2) is characterized by the salting out capacity of $Ca(NO_3)_2$. The eutonic point of the solution of these salts cannot be determined experimentally, since the saturation curve of $Ba(NO_3)_2$ approaches extremely closely to the $Ca(NO_3)_2$ ordinate without breaks. Obviously, the eutonic point lay somewhat lower. *

We determined the composition of Solution II approximately, since the $BaCl_2$ saturation curve in Fig. 4 most closely, without breaks, approached the $CaCl_2$ ordinate, and the experimental determination of the eutonic point by the visual-polythermal method was accompanied by a large experimental error.

As is evident in Fig. 5, on the diagram the internal profile presented three branches, which intersected the regions of crystallization of $Ba(NO_3)_2$, $BaCl_2$, $CaCl_2$.

On the basis of the data obtained it was possible to construct 80,100 and 120° isotherms of the reciprocal system $Ba^{\cdot\cdot}$ $Ca^{\cdot\cdot} \| Cl', NO_3'-H_2O$, on the whole, as a projection of the surface of crystallization of the system onto a square (Figs. 6,7,8).

It is possible to make an inference concerning the extremely low solubility of $Ba(NO_3)_2$ in the presence of calcium chloride and nitrate under the temperature conditions which we studied. Our system was reversibly reciprocal in the presence of even small quantities of water at 80, 100 and 120°.

From the practical point of view the fact that, as a consequence of their high solubility, $CaCl_2$ and $Ca(NO_3)_2$ are excellent salting out agents for $Ba(NO_3)_2$, is extremely important. As is evident from Table 7, in a temperature range of 80-120°, isothermal Solution I contains from 1.66-1.76 mole % of $Ba(NO_3)_2$ and from 15.84-16.74 mole % of $Ca(NO_3)_2$. In Solution II at the same temperatures there is less than 0.14 mole % of $Ba(NO_3)_2$ and less than 1.36 mole % of $Ca(NO_3)_2$.

* Unlike the melts of the present system [6], in the presence of water the compound $CaCl_2 \cdot BaCl_2$ is absent.

TABLE 1

Solubility of the Salts in the Systems $Ba(NO_3)_2-BaCl_2-H_2O$ and $Ba(NO_3)_2-Ca(NO_3)_2-H_2O$

System of salts	Salt contents in solution (in mole %)		80° isotherm		100° isotherm		120° isotherm	
	Salt I	Salt II	Moles of H_2O for dry residue of 100 moles	Solid phases	Moles of H_2O for dry residue of 100 moles	Solid phases	Moles of H_2O for dry residue of 100 moles	Solid phases
$BaCl_2-H_2O$	-	100.0	2143.0	$BaCl_2 \cdot H_2O$	1970.7	$BaCl_2$	1845.2	$BaCl_2$
I	16.60	80.40	1783.0		-		1534.2	
	25.47	74.53	-		1388.1		1288.5	
$Ba(NO_3)_2-$	30.04	69.96	1789.0		1349.8		1221.1	
II	34.70	65.30	2131.9		1665.7		1260.2	
$BaCl_2-H_2O$	44.35	55.65	-		-		1673.7	
	54.48	45.52	3558.8	$Ba(NO_3)_2$	2568.2	$Ba(NO_3)_2$	1975.0	$Ba(NO_3)_2$
	65.02	34.98	4268.0		3095.0		2266.4	
	76.12	23.88	4898.0		3552.3		2565.7	
$Ba(NO_3)_2-H_2O$	100.0	-	6603.0		4130.0		3229.3	
$Ba(NO_3)_2-H_2O$	100.0	-	6603.0		4136.0		3229.3	
	41.49	28.51	-		4067.0		-	
	59.51	40.49	-		3772.5		2863.3	
I	48.57	51.43	4752.0		3341.0		2646.4	
$Ba(NO_3)_2-$	29.53	70.47	4022.0	$Ba(NO_3)_2$	2807.0	$Ba(NO_3)_2$	2230.8	$Ba(NO_3)_2$
II	21.19	78.81	3515.9		2507.9		1981.5	
$Ca(NO_3)_2-$	13.58	86.42	2657.4		1980.7		1578.9	
H_2O	6.54	93.46	2049.8		1384.8		1030.1	
	3.68	96.32	894.4		620.1		500.0	
$Ca(NO_3)_2-H_2O$	-	100.0	142.3	$Ca(NO_3)_2$	140.2	$Ca(NO_3)_2$	137.9	$Ca(NO_3)_2$

TABLE 2

Composition of Eutonic Solutions

Systems	Isotherms	Salt contents (in mole %)		Moles of H_2O for dry residue of 100 moles	Solid phases
		$Ba(NO_3)_2$	$BaCl_2$		
$Ba(NO_3)_2-BaCl_2-H_2O$	80°	26.0	74.0	1600.0	$Ba(NO_3)_2 + BaCl_2 \cdot H_2O$
	100°	28.5	71.5	1320.0	$Ba(NO_3)_2 + BaCl_2$
	120°	30.0	70.0	1180.0	
		$Ba(NO_3)_2$	$Ca(NO_3)_2$		
$Ba(NO_3)_2-Ca(NO_3)_2-H_2O$	80°	<0.10	>99.90	<142.3	$Ba(NO_3)_2 + Ca(NO_3)_2$
	100°	<0.10	>99.90	<140.9	
	120°	<0.10	>99.90	<137.9	

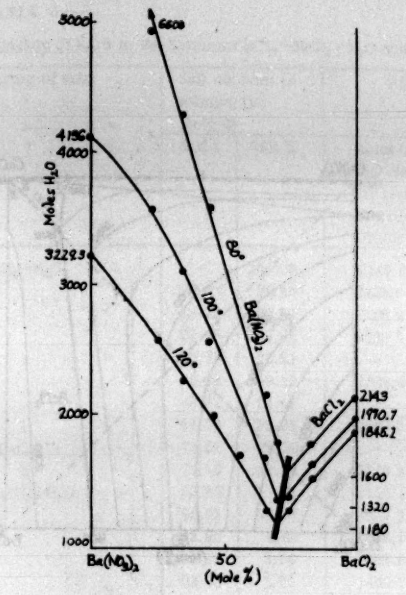

Fig. 1. Solubility isotherms of ternary system of barium nitrate, barium chloride and water.

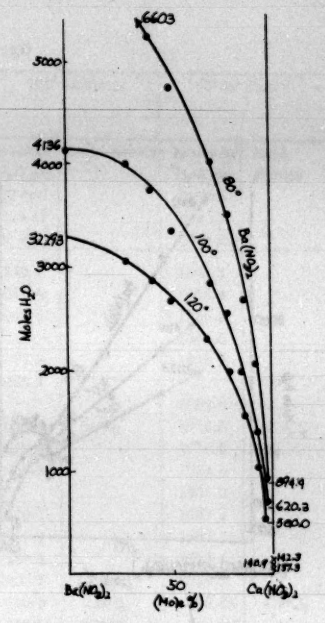

Fig. Solubility isotherms of ternary system of barium nitrate, calcium nitrate and water.

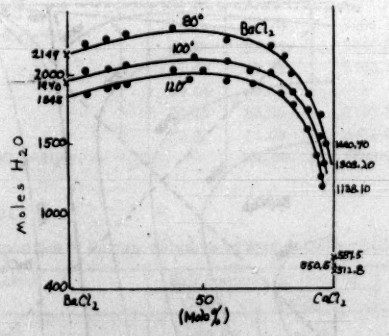

Fig. 3. Solubility isotherms of the system of barium chloride, calcium chloride and water.

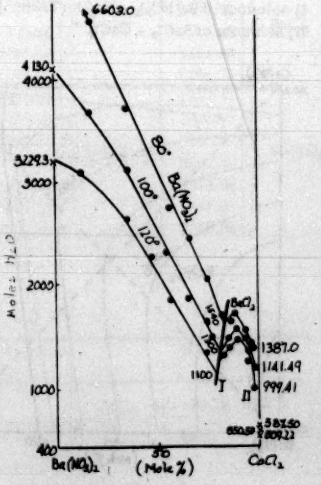

Fig. 4. Solubility isotherms of the system calcium chloride, barium nitrate and water.
I) Solutions of $Ba(NO_2)_2 + BaCl_2$ (Table 5);
II) Solutions of $BaCl_2 + CaCl_2$ (Table 5).

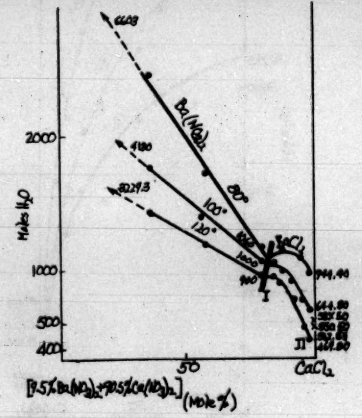

Fig. 5. Solubility isotherms of system
{[9.50% $Ba(NO_3)_2$ + 90.50% $Ca(NO_3)_2$] + $CaCl_2$} → H_2O
I) Solutions of $Ba(NO_3)_2$ + $CaCl_2$ (Table 7);
II) Solutions of $BaCl_2$ + $CaCl_2$.

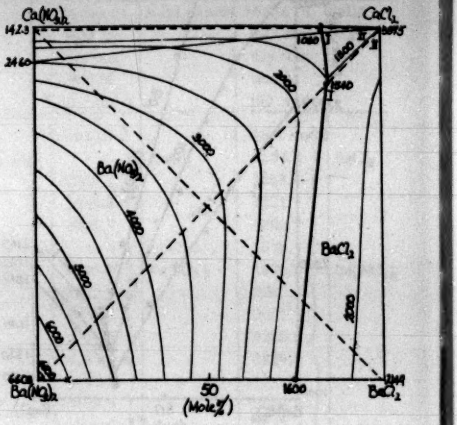

Fig. 6. Projection of 80° solubility isotherm of the reciprocal system $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ ‖ Cl', NO_3'–H_2O. Elucidation in text.

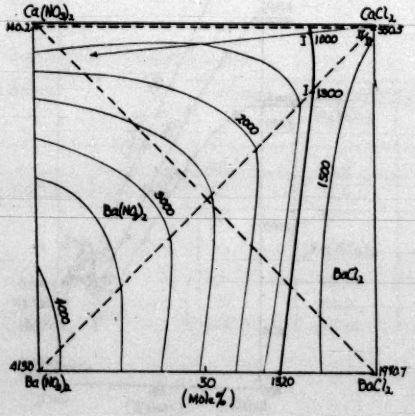

Fig. 7. Projection of the 100° solubility isotherm of the reciprocal system $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ ‖ Cl', NO_3'–H_2O. Elucidation in text.

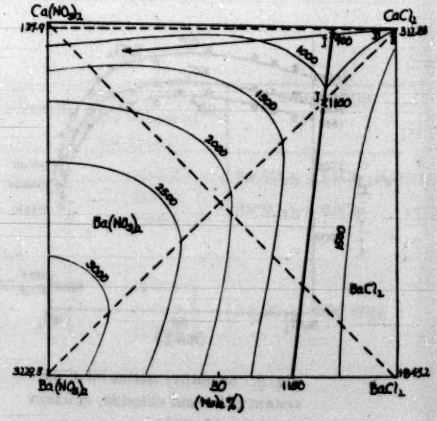

Fig. 8. Projection of the 120° solubility isotherm of the reciprocal system $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$ ‖ Cl', NO_3'–H_2O. Elucidation in text.

TABLE 3

Solubility of Salts in the Systems $CaCl_2-BaCl_2-H_2O$ and $CaCl_2-Ba(NO_3)_2-H_2O$

Systems of salts	Salt contents in solution (in mole %)		80° isotherm		100° isotherm		120° isotherm	
	Salt I	Salt II	Moles of H_2O per dry residue of 100 moles	Solid phases	Moles of H_2O per dry residue of 100 moles	Solid phases	Moles of H_2O per dry residue of 100 moles	Solid phases
$BaCl_2-H_2O$	-	100.00	2149.0		1970.7		1845.2	
	7.84	92.16	2238.9		2021.4		1886.4	
	15.19	84.81	2258.2		2041.5		1915.0	
	22.15	77.85	2298.9		-		1941.0	
	20.77	79.21	-		2077.5		1946.9	
	40.88	59.12	2322.4		2058.9		-	
	48.92	51.08	-		-		1992.7	
I	61.78	38.22	2289.5	$BaCl_2 \cdot H_2O$	2079.4	$BaCl_2$	1970.8	$BaCl_2$
$CaCl_2$ -	71.61	28.39	-		2037.5		1936.6	
II	79.56	20.44	2213.9		2014.8		1924.5	
$BaCl_2-H_2O$	82.89	17.11	2118.1		-		1875.0	
	86.62	13.38	2033.3		1870.9		1757.7	
	93.60	6.40	1838.1		1706.2		1582.7	
	96.86	3.14	1686.8		1529.1		1395.1	
	98.73	1.27	1440.7		1303.2		1138.1	
$CaCl_2-H_2O$	100.00	-	587.5	$CaCl_2 \cdot H_2O$	550.5	$CaCl_2$	512.83	$CaCl_2$
$CaCl_2-H_2O$	100.00	-	587.5	$CaCl_2 \cdot H_2O$	550.50	$CaCl_2$	519.82	$CaCl_2$
	99.02	0.08	1387.0		1141.49		999.41	
	97.45	2.55	1399.9		1355.80		1261.90	
	94.81	5.19	1554.4		1495.14		1430.72	
	88.99	11.01	1709.4	$BaCl_2 \cdot H_2O$	1570.90	$BaCl_2$	1451.38	$BaCl_2$
I	85.88	14.12	9607.5		1471.40		1391.20	
$CaCl_2$ -	82.52	17.48	1651.4		1371.49		1298.70	
II	74.25	24.75	2059.1		1631.20		1317.41	
$Ba(NO_3)_2-H_2O$	66.96	33.04	2448.8		1898.50		1532.08	
	57.44	42.58	2760.4		2246.60		1843.97	
	46.44	53.54	-	$Ba(NO_3)_2$	-	$Ba(NO_3)_2$	2224.89	$Ba(NO_3)_2$
	36.25	63.75	3705.0		3126.90		2674.98	
	18.37	81.63	4498.8		3667.20		3043.81	
$Ba(NO_3)_2-H_2O$	-	100.00	6603.0		4130.00		3229.30	

TABLE 4

Composition of Eutonic Solutions of System $CaCl_2-BaCl_2-H_2O$

Isotherms	Salt contents (in mole %)		Moles of H_2O per 100 moles of salts of dry residue	Solid phases
	$CaCl_2$	$BaCl_2$		
80°	>99.90	<0.10	587.50	$CaCl_2 \cdot H_2O + BaCl_2 \cdot H_2O$
100°	>99.90	<0.10	550.53	$CaCl_2 + BaCl_2$
120°	>99.90	<0.10	512.83	

TABLE 5

Composition of Solutions Saturated with Several Salts in the System $CaCl_2$–$Ba(NO_3)_2$–H_2O

Isotherms	Solution I				Solution II			
	Salt contents (in mole %)		Moles of H_2O per dry residue of 100 moles	solid phases	Salt contents (in mole %)		Moles of H_2O per dry residue of 100 moles	Solid phases
	$Ba(NO_3)_2$	$CaCl_2$			$Ba(NO_3)_2$	$CaCl_2$		
80°	15.0	85.0	1540.0	$Ba(NO_3)_2 + BaCl_2 \cdot H_2O$	<0.08	>99.02	587.50	$BaCl_2 \cdot H_2O + CaCl_2 \cdot H_2O$
100°	17.5	82.5	1340.0	$Ba(NO_3)_2 +$	<0.08	>99.02	550.50	$BaCl_2 + CaCl_2$
120°	18.5	81.5	1170.0	$+ BaCl_2$	<0.08	>99.02	512.83	

TABLE 6

Internal Profile: $\{[9.5\%\ Ba(NO_3)_2 + 90.5\%\ Ca(NO_3)_2] + CaCl_2\} \rightarrow H_2O$

Systems of salts	Salt contents (in mole %)		80° isotherm		100° isotherm		120° isotherm	
	$CaCl_2$	$Ca(NO_3)_2 + Ba(NO_3)_2$	Moles of H_2O per dry residue of 100 moles	Solid phases	Moles of H_2O per dry residue of 100 moles	Solid phases	Moles of H_2O per dry residue of 100 moles	Solid phases
$CaCl_2$–H_2O	100.00	-	587.5	$CaCl_2 \cdot H_2O$	550.50	$CaCl_2$	512.83	$CaCl_2$
	98.50	1.50	944.4		664.60		469.80	
	96.20	3.80	1058.8		743.70		538.70	
	92.37	7.63	1077.0	$BaCl_2 \cdot H_2O$	897.00	$BaCl_2$	749.70	$BaCl_2$
$\{[9.5\%\ Ba(NO_3)_2 +$	88.42	11.58	1118.2		998.80		897.60	
$+ 90.5\%\ Ca(NO_3)_2] +$	84.28	15.72	1084.7		1003.90		932.00	
$+ CaCl_2\} \rightarrow H_2O$	80.10	19.90	1130.7		1027.40		1172.40	$Ba(NO_3)_2$
	57.38	-	1768.4	$Ba(NO_3)_2$	1398.50	$Ba(NO_3)_2$	1408.30	
	36.58	63.42	2450.2		1762.40			

TABLE 7

Composition of Isothermal Solutions Saturated with Several Salts

Isotherms	Solution I					Solution II				
	Salt contents (in mole %)			Moles of H_2O per dry residue of 100 moles	Solid phases	Salt contents (in mole %)			Moles of H_2O per dry residue of 100 moles	Solid phases
	$CaCl_2$	$Ba(NO_3)_2$	$Ca(NO_3)_2$			$CaCl_2$	$Ba(NO_3)_2$	$Ca(NO_3)_2$		
80°	82.50	1.66	15.84	1060	$BaCl_2 \cdot H_2O + Ba(NO_3)_2$	>98.5	<0.14	<1.36	587.5	$BaCl_2 \cdot H_2O + CaCl_2 \cdot H_2O$
100°	82.00	1.71	16.29	1000	$BaCl_2 +$	>98.5	<0.14	<1.36	550.5	$BaCl_2 +$
120°	81.50	1.76	16.74	900	$+ Ba(NO_3)_2$	98.5	0.14	1.36	469.8	$+ CaCl_2$

SUMMARY

1. The solubility of salts of a quadruple reciprocal system of the chlorides and nitrates of barium and calcium was studied by the visual-polythermal method at 80, 100 and 120°.

2. On the solubility diagram (at 80-120°), unlike the fusibility diagrams, in the system $CaCl_2-BaCl_2-H_2O$ no compounds were detected.

3. It was found that on the solubility diagram the reciprocal system $Ba^{++}, Ca^{++} \quad Cl', NO_3'-H_2O$ at 80-120° is reversibly-reciprocal.

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* T. p. = C. B. Translation pagination.

PREPARATION AND SOME PHYSICO CHEMICAL PROPERTIES OF AMMONIUM LUTEOPHOSPHOMOLYBDATE

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The unsaturated hetero-polyacids and their salts have still been very inadequately studied, therefore, developing a method of production of free luteophosphomolybdic acid [1], we investigated in detail the methods of production of its ammonium salt, and then studied the solubility and viscosity of the latter. The study of the physico-chemical properties of ammonium luteophosphomolybdate (it will be written as l.p.m. subsequently) was carried out also for practical considerations; it enabled us to establish that some nitrogen-containing organic bases, for example, quinoline, form insoluble salts with l.p.m. acid, whereas the ammonium l.p.m. itself is quite highly soluble in water. A systematic study of the solubility of ammonium l.p.m. verified the possibility of the use of l. p. m. acid as a reagent for the detection of different amines in the presence of ammonium ion.

Kermann observed the formation of ammonium l.p.m. for the first time [2] by the action of ammonium chloride on a solution of saturated phosphomolybdic acid which had stood for several months (it will be written as s.p.m. subsequently); the latter formed only a negligible precipitate of ammonium s.p.m., retaining at this time its intense yellow color. Kermann drew the conclusion, based on this observation, that the new l.p.m. acid which formed on standing of s.p.m. acid formed a soluble ammonium salt. Kermann established that the composition of this salt corresponded to the formula $3(NH_4)_2O \cdot P_2O_5 \cdot 18MoO_3 \cdot 14H_2O$.

EXPERIMENTAL

In our first experiments ammonium l.p.m. was obtained by the neutralization method. A titrated solution of ammonium hydroxide (0.0194 g NH_3 in 1 ml) and a solution of l.p.m. acid containing 20.565 g of the anhydrous compound in 100 ml were prepared for this purpose. The calculated quantity of NH_4OH solution, required for the formation of the hexa-substituted salt was added dropwise from a burette to the solution of the acid in the cold.

$$(NH_4)_6H_6\left[\begin{array}{c} P(MoO_7)_4\,(Mo_2O_7)_4P \\ O \quad\quad Mo_2O_7 \quad\quad O \end{array}\right] \cdot H_2O$$

After introduction of the required amount of ammonium hydroxide solution, we observed that the resulting solution of l.p.m. salt became golden-yellow from orange-yellow; after careful stirring the solution was placed in a desiccator with H_2SO_4 for isothermal crystallization at room temperature. After several days a precipitate of ammonium s.p.m. came down from the solution, which was filtered off, and the solution was again set up for crystallization; a precipitate of ammonium s.p.m. again formed after a short time. It was observed that, in proportion to the evaporation of the solution, the quantity of ammonium s.p.m. precipitate which came down increased, and crystals of ammonium l.p.m. were not formed at all. The quantity of ammonium s. p. m., which separated indicated only an incomplete conversion of ammonium l. p. m. to the salt of s. p. m. acid; apparently, the neutralization of l. p m. acid by ammonium hydroxide until the formation of the hexa-substituted salt caused its partial conversion to the corresponding salt of s. p. m. acid, and in the solution the following equilibrium was established.

$$2(NH_4)_6H_6[P_2O_2(Mo_2O_7)_5] \rightleftharpoons 3(NH_4)_3H_4[P(Mo_2O_7)_6] + (NH_4)_3PO_4.$$

Since we were unable to prepare ammonium l.p.m. by the neutralization method, in the second series of experiments we obtained the salt from l.p.m. acid and ammonium chloride; an impurity of about 1% of s.p.m. acid, which was in the initial l.p.m. acid, was precipitated as ammonium s.p.m. by a small quantity of ammonium chloride, and was removed by filtration. After removal of the ammonium s.p.m. an excess of a saturated solution of ammonium chloride was added to the clear filtrate, and after careful stirring the l.p.m. salt was crystallized isothermally over H_2SO_4 in a desiccator. After several days (3-5), a small quantity of well-formed rhombohedral crystals of ammonium l.p.m. of an orange-yellow color precipitated; however, both the bottom of the crystallizer and the crystal surfaces were covered with a fine powder of ammonium s.p.m. After recovery of the first fraction of crystals the solution was filtered off, and it was again isothermally evaporated in order to produce the next crystal fractions; however, again the resulting crystals were covered with a fine layer of ammonium s.p.m.

The 32 g of salt obtained by isothermal crystallization was recrystallized from water in order to remove the traces of Cl^-; however, under the conditions of this repeated isothermal crystallization, the preparation which was freed from Cl^- was also covered with a thin film of ammonium s.p.m. Apparently, here also, although to a lesser extent than under the conditions of the first series of experiments, the reverse conversion of ammonium l.p.m. to the salt of the saturated acid occurred.

Analysis of Salt Obtained

Found %: P_2O_5 4.92; $(NH_4)_2O$ 5.48; MoO_3 89.60. $3(NH_4)_2O \cdot P_2O_5 \cdot 18MoO_3$. Calculated %: P_2O_5 4.91; $(NH_4)_2O$ 5.40; MoO_3 89.69.

In the third series of experiments the preparation of ammonium l.p.m. was carried out by the action of a concentrated solution of ammonium chloride on l.p.m. acid, and the l.p.m. acid was also used in a higher concentration.

45-50% solutions of l.p.m. acid were prepared; equal volumes of a saturated solution of ammonium chloride were added to them. On pouring these solutions together a voluminous precipitate of ammonium l.p.m. formed immediately as fine, clear, orange crystals. The salt was filtered off onto a funnel; the preparation contained a considerable quantity of chlorine. On removal of Cl^- by recrystallization from water under isothermal conditions, again a partial formation of the ammonium salt of the saturated acid took place.

In the fourth series of experiments ammonium l.p.m. was prepared, and was purified by recrystallization from alcohol. We were able to establish that, unlike the s.p.m. acid, l.p.m. acid and its ammonium salt are highly solubie in alcbhol. The use of alcohol as the solvent must be eliminated for the reverse reaction—the conversion of l.p.m. acid to the saturated acid.

We used a 30% solution of l.p.m. acid, and the impurity of s.p.m. acid amounted to ~1%. The first operation consisted, as described above, in the removal of the s.p.m. acid by a small quantity of ammonium chloride; an equal volume of ammonium chloride was added to a solution of l.p.m. acid, freed of its impurity of the saturated form. The resulting solution of ammonium l.p.m. was left for 2 days, after which a considerable quantity of coarse, orange rhombohedral crystals of ammonium l.p.m. covered by a yellow film of the salt of s.p.m. acid, was formed. The crystals were filtered off and dissolved in alcohol; the alcoholic solution of ammonium l.p.m. was filtered off from the insoluble precipitate of the salt of s.p.m. acid and placed in a vacuum desiccator for evaporation (water-jet pump). No crystal formation was observed after 18 hours of evaporation, and the solution was left for crystallization in the air. After a day the recovered (green color) crystals of ammonium l.p.m., and simultaneously a small quantity of the salt of s.p.m. acid, were formed, whereupon in the alcoholic medium a decrease of the quantities of this impurity was observed. For the production of ammonium l.p.m. freed of traces of s.p.m. acid, it was necessary to accelerate the process of crystallization of ammonium l.p.m. from alcohol, since slow formation of the preparation leads to the formation of an ammonium s.p.m. impurity.

For this purpose ether was added to an alcoholic solution of ammonium l.p.m., and, after stirring, was poured into the heavier alcoholic solution of the salt. The operation of the addition of ether was repeated 4-5 times. Each portion of ether extracted additional quantities of alcohol, the solution of ammonium l.p.m. became more and more saturated and, finally the crystalline salt precipitated from it. Decanting the last portion of ether from the crystals, we then transferred them to a sheet of filter paper. After evaporation of the traces of ether the dry crystals were dissolved in water without any turbidity: the ammonium s.p.m. impurity had been eliminated.

Analysis of the Ammonium L.p.m. Obtained

Found %: P_2O_5 5.10: $(NH_4)_2O$ 5.36: MoO_3 89.70. $3(NH_4)_2O \cdot P_2O_5 \cdot 18MoO_3$. Calculated %: P_2O_5 4.91; $(NH_4)_2O$ 5.40; MoO_3 89.69.

The salt was prepared for further physico-chemical investigations by the method indicated.

Study of the System Ammonium L.p.m. – Water at 20° by the Viscometric Method

The determination of the specific gravity and viscosity at 20° was carried out in a glass thermostat equipped with a stirrer. An Ostwald viscometer was used for measurement of the viscosity. The empty apparatus was kept in the thermostat at the temperature of the experiment for 30 minutes, after which the solution to be tested was poured into it and the time of its discharge was determined by a stopwatch. First determining the time of discharge of the same volume of water at 20°, we calculated the viscosity from the formula

$$\eta = \eta_0 \frac{dt}{d_0 t_0},$$

where η_0 is the viscosity of water in poises at the given temperature, d and t are the specific gravity and the rate of discharge of the solution investigated, and d_0 and t_0 are the same values for water.

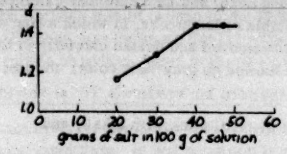

Fig. 1. Specific gravity of solutions of ammonium luteophosphomolybdate.

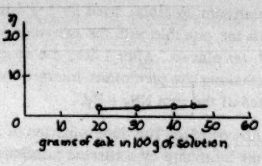

Fig. 2. Viscosity of solutions of ammonium luteophosphomolybdate.

Graphs of the relation of the specific gravities and the viscosities to the concentration were constructed on the basis of the data of Table 1. As is evident from Figs. 1 and 2, this relationship has a linear character.

TABLE 1

Specific Gravity and Viscosity of the System Ammonium l.p.m.–Water at 20°

Concentration of solution (in %)	Specific gravity	Viscosity
19.93	1.1776	1.2255
30.89	1.3064	1.4136
41.03	1.4482	1.7048
46.26	1.4491	1.7025

TABLE 2

Solubility of Ammonium l.p.m. in Water

Temperature	Anhydrous salt content (in grams/100 g of solution)	H_2O content in solid phase (in %)	(in moles)
0	34.46	17.86	
5	37.88	16.84	
10	-	-	
15	45.06	17.78	
20	48.90	17.65	about 25–27
25	50.74	17.93	
30	53.64	17.93	
35	55.95	-	
40	58.93	18.06	
45	considerable decomposition		

The linear character of the viscosity isotherms indicates the absence of chemical reaction of the components in the solution studied.

Study of the Solubility in the System Ammonium l.p.m. – Water

We used a thermostat with temperature fluctuations of ±0.1° for the solidity study. Equilibrium was attained after 2-3 hours. Selection of a sample of the liquid phase for analysis was made by means of a pumping pipette; for selection of a sample of the solid phase about 1 g of the crystals were recovered from the bottom of the vessel, dried quickly with filter paper, weighed and calcined to constant weight.

The hydrated form of ammonium l.p.m., with a content of about 25-27 molecules of water of crystallization, existed in the range from 0 to 45° Partial decomposition of the salt with formation of H_2MoO_4, took place at 40°, reaching considerable amounts at 45° (Table 2).

Analytical. The analysis of ammonium l.p.m. included the determinations of NH_3, H_2O, the sum $P_2O_5 + MoO_3$ and P_2O_5. The method of determination of P_2O_5 and MoO_3 was described earlier [3].

For the determination of the sum $NH_3 + H_2O$ a weighed portion of the substance, about 1 g, was placed in a porcelain or platinum crucible, dried for 1-1.5 hours at 100-110° in a drying oven, and then carefully calcined at 30°. For this the crucible with the substance was placed in another crucible of larger size, in which a ring of asbestos board was placed. After 1 hour the crucible and the substance were removed and heated carefully in the burner flame (shaking the precipitate intermittently) until the precipitate showed no gray-blue color; the loss in weight consisted of the sum $NH_3 + H_2O$.

Determination of NH_3. The determination of ammonia was carried out by distillation with alkali, and collection of the ammonia by a titrated solution of sulfuric acid.

SUMMARY

1. Hexa-substituted ammonium l.p.m. was formed by the action of an excess quantity of ammonium chloride on a solution of l.p.m. acid. Under the conditions of isothermal crystallization the preparation obtained was contaminated by ammonium s.p.m.; a similar difficulty with somewhat smaller amounts was observed on slow crystallization from alcohol.

2. Ammonium l.p.m. of exact composition was obtained by the reaction of concentrated solutions of l.p.m. acid and ammonium chloride; the pressed salt was dissolved quickly in alcohol and was separated in the crystalline state by shaking with ether.

3. The viscosity of ammonium l.p.m. was studied at concentrations from 20% to saturation.

4. The solubility of ammonium l.p.m. was studied from 0° to the beginning of decomposition of the salt.

5. It was found that within these temperature limits the solid phase is the hydrated form with a content of about 25-27 moles of water.

6. Decomposition of the saturated solutions of ammonium l.p.m. began at 40°.

7. It was found that the viscosity and specific gravity curves have a linear character.

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CHEMISM OF THE FORMATION OF PHOSPHORESCENCE CENTERS IN ZINC SULFIDE PHOSPHORS

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The decisive role of oxygen in the formation of some zinc sulfide phosphors, particularly non-activated ZnS-phosphor, was shown earlier [1]. The crystal chemistry of a model of the phosphorescence centers of zinc sulfide phosphors, based both on previous and on new experimental data, is proposed in the present paper.

1. Models of Centers of Phosphorescence

From investigations [2,3] it became known that copper may exist as an activator in ZnS-phosphors in two different conditions. In one condition it gives the usual green phosphorescence, but in the other it gives dark blue. The "green" state of copper exists chiefly at low copper contents in the phosphor, but the "dark blue" exists at high copper contents.

The activator is added not only before calcination of the phosphor, but also by diffusion [4] into the prepared sulfide crystal particles at 300-500°. Entirely different results were obtained by diffusion of 10^{-4} g of copper per 1 g of prepared crystalline ZnS at 450°, depending on the condition of the crystalline sulfide, into which the introduction was made [3]. If the indicated quantity of copper was introduced into the ordinary non-activated zinc sulfide calcined at 850° and giving a bright azure phosphorescence, final preparations with the ordinary green phosphorescence inherent to the ZnSCu phosphor were obtained. If the same quantity of copper, under the same conditions, was diffused into non-activated zinc sulfide, calcined at 1250° and giving only an extremely weak azure phosphorescence, final preparations with a strong dark blue copper phosphorescence were obtained. The green phosphorescence was obtained here only by a decrease of the addition of copper (about 10^{-5} g of Cu per 1 g of ZnS).

Thus, not only the quantity of copper introduced, but also the initial condition of the ZnS-crystals themselves, predetermined whether copper was introduced as " green" or as "dark blue" phosphorescence centers. In the ZnS-crystal, again before the introduction of copper, there must exist those structural characteristics (acceptors), which determine the readiness of the crystal to absorb copper as "green" centers. If there are few such acceptors in the crystal considered, the crystal may absorb only a small amount of copper as "green" centers. The introduction of additional quantities of copper by diffusion leads to the additional formation of "dark blue" centers only.

The "green" centers cannot develop simply by the introduction of copper into the interstices of the normal lattice. For this, the fact has already been stated that the readiness of the zinc sulfide to form "green" centers depends to a high degree on the thermal history of the original crystal. The following is a direct demonstration of this. We effected the introduction of copper by diffusion into ZnS-crystals for which, regardless of conditions, we would not expect deviations from the ZnS stoichiometric formula. These were Zns-crystals obtained by calcination of precipitated zinc sulfide in a current of H_2S at different temperatures (900-1200°). Both from the nature of the method of preparation itself [5], and also from the results of the most accurate analyses of the product, it could be assumed that we could obtain zinc sulfide of irreproachable stoichiometric composition by this method; this was confirmed again also by the fact that the zinc sulfide obtained by this method showed no characteristics of visible luminescence. On introduction of copper into such zinc sulfide by diffusion a preparation formed which showed none of the characteristics of green or dark blue luminescence of copper. Thus, neither the normal defect-free lattice nor the interstices of the normal zinc sulfide lattice were able to absorb copper in the luminescent condition. Only the defective, imperfect spots of the ZnS-lattice were able to absorb copper as phosphorescence centers.

Since in the crystals (without deviation from the formula) neither centers with green nor with dark blue phosphorescence developed, the presence of anomalous spots or acceptors was a necessary condition, not only for the formation of "green" centers, but also for "dark blue" centers.

We again observed a parallelism between the intensity of the azure luminescence of non-activated zinc sulfide and its capacity to absorb copper as green phosphorescence centers, indicating the source of a relation between the centers responsible for the azure phosphorescence of non-activated zinc sulfide and the above-mentioned acceptors. From the above it is obvious that there are some anomalous spots in the lattice of the non-activated

crystalline zinc sulfide (with azure luminescence) which are able to react with copper and form phosphorescence centers with it, independent of whether copper was present during the development of these anomalies. These reformed anomalies (acceptors) are a necessary condition for the formation of both Cu-centers of green phosphorescence and also for Cu-centers of dark blue phosphorescence.

What is the nature of these lattice imperfections (acceptors)? A certain excess of zinc is separated by the thermal decomposition of the zinc sulfide to residual sulfide. This gives us the right to assume that in the zinc sulfide S-defects may develop, i. e., holes remaining from the removal of sulfur atoms (Fig. 1). From the crystallochemical point of view, such an assumption is natural and plausible.

Although thermal decomposition [6] by itself is an irrefutable fact, just the same some care should be exercised in the deductions concerning the condition of the sulfide which remains in the crucible after calcination. It can be imagined that dissociation leads to the formation of S-defects in the lattice (holes, which remain from the removal of sulfur atoms). But since, at the temperatures considered, elementary zinc also has a great volatility (at 900°, 1 atm), it can be assumed that the decomposition of the zinc sulfide in general does not lead to stoichiometric deviations in the lattice of the residual sulfide, i. e., that both of the decomposition products (both the sulfur and the zinc) are volatilized completely. Further, it can be assumed that the free Zn-atoms which form on dissociation (owing to the small diameter of these atoms) in the interstices of the ZnS-crystal also form in them an excess of zinc. Finally, it can be imagined that in the ZnS-lattice there remain neither defects nor an excess of atoms, but that in the strictly stoichiometric total composition, some other lattice imperfections remain in the crystal, for example, zinc atoms displaced from the nodes of the lattice into the internodes. Many experiments on the thermal decomposition of zinc sulfide were carried out in vacuo. Non-activated ZnS-phosphor with an azure phosphorescence was used as the object. This sulfide was calcined for different lengths of time in vacuo (10^{-3}–10^{-4} mm) at different temperatures between 500 and 1100°. Calcination proceeded without the addition of flux or any other foreign substances. If the thermal decomposition took place at not too high temperatures (500-900°), the sulfide which remained in the crucible (quartz boat) after calcination was of a blackish-gray color. It contained a considerable quantity of non-volatile, elementary zinc, which was not leached by acids; consequently, this zinc was not located on the surfaces of the sulfide grains. The higher the experimental temperature, the less the excess of elementary zinc which remained in the sulfide; an entirely white product was obtained only by calcination above 1050°. The difficulty of removal of the excess zinc by calcination indicated that the elementary zinc which formed in the zinc sulfide was volatilized to a smaller extent than was the ordinary metallic zinc, which volatilized almost instantaneously at the temperatures specified.

Again we observed that, for the samples of non-activated phosphor which we used, the azure luminescence underwent almost no weakening on calcination in vacuo; in spite of the fact that the sample became gray as a result of the formation of free zinc, the brightness of the luminescence was reduced only to such an extent as was explained by the simple optical absorption of light by the gray deposit.

The problem concerning the state of the excess zinc which accumulated in the residual sulfide as a result of the thermal decomposition of the latter (also, the accumulation of Zn-atoms in the internodes, the formation of S-defects, and the formation of colloidal zinc particles are possible) remained unsolved. It is only certain that, by a purely thermal dissociation of the zinc sulfide, an excess of zinc actually forms in the residual sulfide, and that this excess becomes smaller the higher the calcination temperature.

Further experiments showed that an excess of zinc also formed in the sulfide on calcination of the purest zinc sulfide in a current of anhydrous HCl. Consequently, the chlorination of the zinc sulfide led not only to the formation of $ZnCl_2$, but also to the formation of a certain amount of excess, elementary zinc. The chemism of this fact is still not at all clear, but the very fact was so accessible to direct observation, that no doubts were aroused. This observation, and also the fact that careful sulfurization of the zinc sulfide rendered it unable to form phosphorescence centers, forced us to assume that: 1) S-defects were responsible for the capacity of the ZnS-crystals to form phosphorescence centers and 2) chlorinating reagents, e.g. HCl, promoted the formation of S-defects.

The formation of an S-defect was equivalent to the appearance of a neutral Zn-atom (or a partially discharged Zn-ion). In Fig. 1 the holes which remained from the removal of a sulfur atom are designated by the symbol of a square, and the neutral zinc atom (or the partially discharged ion) is designated by the symbol Zn. This entire anomalous spot of the lattice will subsequently be designated [Zn][ ]-center*.

We can assume that the [Zn][ ]-center by itself does not yield phosphorescence. In any case it gives no azure phosphorescence of the non-activated zinc sulfide, because neither purely thermal desulfurization nor desulfurization

* We made no attempt to predetermine the problem of the actual distribution of electrons among the atom, hole and surrounding lattice.

by anhydrous hydrogen chloride produces an azure luminescence.*

According to our data [1], the zinc sulfide which by itself is non-luminous, obtained, for example, by a chlorination calcination in the absence of oxygen, was able to absorb copper in the luminescent condition, for which this copper can be introduced by diffusion into the crystal prepared at 300-500°. We suggest further that the quantity of copper which may be introduced as green phosphorescence centers is limited, and that this quantity is determined by the number of some anomalous points, the acceptors in the ZnS-crystal. This led us to the idea of identifying the acceptors with the [Zn][ ]-centers, and of assuming that the copper was introduced into the [Zn][ ]-centers displacing the zinc atoms from it. Such a type of displacement was very plausible from the chemical point of view, since copper, being a more noble metal than zinc, has a greater tendency to pass into the neutral atomic state than does zinc.

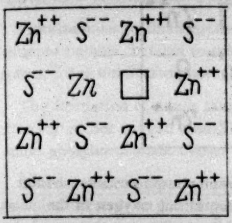

Fig. 1. Model of non-luminous S-defect (acceptor) in the ZnS lattice (The [Zn][ ]-center designated in text).

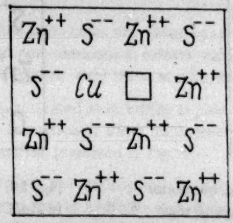

Fig. 2. Model of oxygen-free Cu-center with green phosphorescence (the [Cu][ ]--center designated in text).

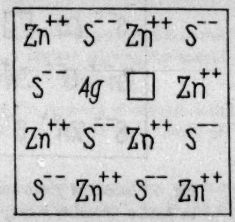

Fig. 2a. Model of oxygen-free Ag-center.

Thus, we concluded that the green phosphorescence center arises from the [Zn][ ]-center on replacement of zinc by copper (Fig. 2). Retaining the symbolism which we assumed, we may designate such a formation by the expression: [Cu][ ]-center. Consequently, the green phosphorescence center of copper is a copper atom (ion) side by side with an S-defect (hole, which remains from a sulfur atom). An entirely analogous structure may be assigned to the ZnSAg phosphor.

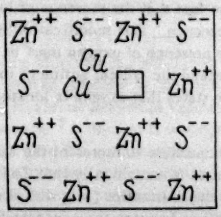

Fig. 3. Model of Cu-center with dark blue phosphorescence (the (Cu)[Cu□]-center designated in text).

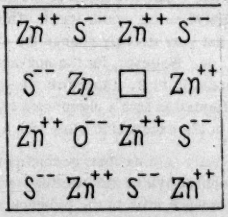

Fig. 4. Model of center of non-activated ZnS-phosphor with azure phosphorescence (the [O][Zn□]-center designated in text).

The question arises of what structure should be ascribed to the dark blue phosphorescence center of copper. It is known that the "dark blue" Cu-centers are formed only by sufficiently large copper contents. Further, we saw that the same anomalous points or "acceptors" are responsible for the formation of "dark blue" Cu-centers as for the formation of the "green" centers. It can be inferred from these conditions that the "dark blue" Cu-centers are formed by the addition of a copper atom to a "green" Cu-center. Second, the additional copper atom is probably located in the interstices (for example, in one of the neighboring vacant tetrahedra between the S-ions) (Fig. 3). Further, we will designate the Cu-centers of dark blue phosphorescence by the formula: (Cu)[Cu□]-center.

We turn to the participation of oxygen in the structure of the phosphorescence centers. In the first place, we saw [1] that the presence of oxygen conditions the formation of the azure phosphorescence centers of non-activated zinc sulfide. In the second place, the presence of oxygen in the ZnS Cu-phosphor appreciably modifies the green phosphorescence of the Cu-centers; the phosphorescence is shifted toward the long waves and becomes yellowish-green, the phosphorescence lasts a long time, the excitability by α-rays decreases and, moreover, a typical change appears in the thermal absorption curves, taken by the method introduced by Kats and repeatedly used in recent years

* In the complete absence of oxygen [1].

[7] (Fig. 6). Similarly, for the ZnSAg-phosphor, Smith [8] observed a clear, although small, long-wave shift of the spectrum, as long as oxygen was present during the preparation. Moreover, it is known that in highly-calcined phosphors oxygen is included in a form inaccessible to leaching, and that for ZnS-wurtzite the isomorphic introduction of ZnO into ZnS should be expected, i. e., the formation of "mixed crystals of replacement" [1]. All this leads to the picture of oxygen-containing phosphorescence centers represented in Figs. 4, 5 and 5a.

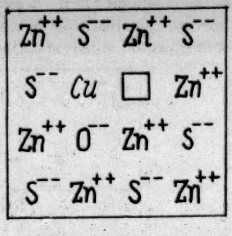

Fig. 5. Model of green phosphorescence center in ZnSCu-phosphor containing oxygen in the lattice (Modification 1).

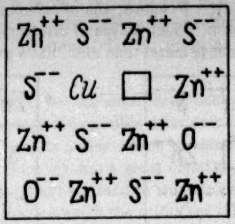

Fig. 5a. Model of green phosphorescence center in ZnSCu-phosphor containing oxygen in the lattice (Modification 2).

We will subsequently designate the azure phosphorescence center of non-activated zinc sulfide: [O][Zn][ ]-center.

The existence of both oxygen-containing and oxygen-free phosphorescence centers can be assumed for the ZnSAg-phosphor, as for the ZnSCu-phosphor. As regards the oxygen-containing centers in ZnSCu- and ZnSAg-phosphors, it should not be maintained that the oxygen occupies a position directly side by side with the center itself. Since for these phosphors we are concerned with large, analytically perceptible oxygen contents, here it is probably more correct to speak of the oxygen atoms distributed in the lattice (instead of sulfur) somewhere around the phosphorescence center itself. This corresponds better to the fact that the presence of oxygen in these instances does not very strongly change the character of the phosphorescence. This modification is represented schematically in Fig. 5a. However, for the non-activated ZnS-phosphor the presence of oxygen must be in the center itself, or in direct proximity to it. Otherwise, it would be difficult to understand the radical action of oxygen, converting a non-luminous formation into a phosphorescence center. The chemism states that oxygen is located preferably exactly side by side with the excess zinc atom, which has two free electrons.

It is necessary to state that, according to our experiments, it is impossible to represent the azure phosphorescence center of the non-activated zinc sulfide itself simply as ZnO introduced isomorphically into ZnS. In no case does the azure phosphorescence arise in the presence of oxygen, except when desulfurization (removal of sulfur) occurs simultaneously. Finally, it is necessary to consider the above-noted parallelism between the concentration of the azure phosphorescence centers in non-activated ZnS-phosphor and the quantity of copper which it is able to absorb as an activator. Consequently, we must also attribute to the "azure" centers the capacity of serving as acceptors. This requirement agrees well with the structure of the centers.

2. Significance of Desulfurization in the Preparation of ZnS-Phosphors*

The desulfurizing action of hydrogen. If the splitting off of sulfur and the formation of [Zn][ ]-centers (acceptors) is required for the formation of a phosphor, it is necessary to attempt to form these acceptors without the help of chlorine, i.e., by the action of some other desulfurizing reagent. Moreover, if we are to prevent oxygen from getting into the phosphor, then a product must be obtained which by itself gives no phosphorescence, but which is able to absorb copper and silver in the luminescent state. . Hydrogen is a reagent which meets these conditions. In the first place, it acts as a desulfurizer, and in the second, it may be obtained in an oxygen-free condition.

Precipitated zinc sulfide, first treated at 500° with gaseous H_2S, and corresponding accurately to the formula ZnS, was calcined in carefully purified hydrogen at 1000° for 1 hour. In the absence of copper an entirely non-luminous preparation was obtained. Only the formation of a preparation with a gray color was observed, as a consequence of the appearance in it of elementary zinc, which indicated the occurrence of a partial desulfurization. (The sulfur hue was observed only if the current of hydrogen was not too strong; with a strong current of hydrogen the gray hue did not

* Phosphors of the ZnSMn type were not considered in the present paper, being "mixed crystals of replacement."

appear, obviously because, as a consequence of the rapid removal of the zinc vapors, a rapid volatilization of the latter occurred and no accumulation of zinc took place. If copper was present, then luminous preparations with all the characteristic properties of the ZnSCu phosphor were obtained. The same were also obtained (although also with a somewhat weaker intensity of phosphorescence) if copper was diffused into a prepared, non-luminous, non-activated product obtained in a hydrogen atmosphere at 450°.

By this it was shown directly that the decisive condition for the formation of phosphorescence centers was the desulfurization of zinc sulfide. Chlorine, as such, was not required, since it showed only an indirect influence, acting, obviously, as a desulfurization reagent.

Simultaneously, this experiment confirmed once more that desulfurization itself still did not lead to the formation of luminous centers, but led to the formation of non-luminous S-defects, called [Zn][ ]-centers, playing the role of acceptors, from which phosphorescence centers formed only if the zinc in them was replaced by copper.

The formation of azure luminescent non-activated zinc sulfide is possible only in the presence of oxygen. Neither desulfurization nor oxygen is sufficient for the formation of azure luminescence. These facts lead to the structure of the azure phosphorescence center of the zinc sulfide presented in Fig. 4.

The desulfurizing action of chlorine. Kröger and Hellingman [9] calcined non-activated zinc sulfide, which corresponded accurately to the formula ZnS, in a current of hydrogen and obtained a non-luminous product.* By the addition of increasing quantities of HCl vapors to the hydrogen these authors obtained products with an intensifying azure phosphorescence. This result contradicted our experiments, since we obtained no azure phosphorescence in HCl vapors in the absence of oxygen. However, Kröger and Hellingman nowhere indicated the use of special measures for removal of the water vapors from the current of hydrogen chloride which they used; therefore, it can be assumed that in Kröger and Hellingman's experiments oxygen was present as H_2O. Thus, it can be understood why Kröger and Hellingman obtained an intensification of the azure phosphorescence with an increase of the HCl concentration, with which an increase of the oxygen concentration (i.e., H_2O vapors) also should be expected. From our experiments, described earlier [1], it is obvious why small quantities of oxygen are sufficient for the formation of the azure luminescence.

In order to eliminate this source of error, we prepared HCl by the action of 98% sulfuric acid on NaCl, dehydrated by fusion. Thus, almost anhydrous HCl vapors formed. (It turned out, however, that not even these measures gave completely anhydrous HCl.

Calcination of the zinc sulfide (900-1150°) was carried out in a current of almost anhydrous HCl vapors; moreover, the purest zinc sulfide obtained by the preliminary reaction of H_2S at 500° was used. None of the products obtained by calcination in almost anhydrous vapors of HCl gave, in contrast to the ordinary non-activated ZnS-phosphor, any azure phosphorescence.** By this it was again confirmed that with a deficiency of oxygen the action of chlorinating reagents does not give the normal azure luminescence of the non-activated zinc sulfide [1]. However, the products calcined in HCl showed the capacity to absorb copper in the luminescent state; as a result of the calcination in HCl, acceptors, [Zn][ ]-centers, formed.

The results of the experiments in HCl vapors still differed essentially from the pattern of the results of those experiments carried out in a current of H_2S in the presence of NaCl; HCl also acted as the reagent, with the difference only that it had to be formed from H_2S and NaCl, and therefore was present in a smaller concentration. Another difference included the fact that [1] much H_2S, which acted as a sulfurizer, was present; here, only that quantity of H_2S was present which was formed from HCl and ZnS. Oxygen was practically absent both here and in [1].

Besides what has been indicated, it was observed that the calcination of pure ZnS in dry HCl vapors led to the formation of free zinc in the zinc sulfide crystals, in a quantity accessible to visual observation. Consequently, together with the usual chlorinating action (leading to the formation of $ZnCl_2$) still another reaction took place, the desulfurization of zinc sulfide, with the formation of free zinc.

The particular effectiveness of all the chlorinating reagents (HCl and chloride fluxes) was explained by this: together with the usual chlorinating action, they brought about a partial removal of sulfur from the ZnS-lattice, with the formation of neutral zinc atoms or [Zn][ ]-centers.

The chemism of the formation of free zinc in the presence of an excess of free HCl was not clear and required special study, but it is less remarkable when it is recalled that the free zinc forms inside the sulfide crystals, i.e., not in direct contact with HCl, and that the zinc sulfide is able persistently to retain in itself free zinc, as experiments on

* They did not carry out further tests of such a non-luminous product for its capacity to absorb copper in the luminescent state.

** Under the condition of a not very high density of excitation. A different result was obtained at a high density excitation.

the thermal decomposition of zinc sulfide in vacuo showed. In connection with what has been represented, it can be concluded that any calcination of zinc sulfide brings about decomposition and desulfurization. However, in the preparation of ZnS-phosphors it is characteristic that crystal growth also occurs simultaneously with desulfurization. Desulfurization takes place on calcination in vacuo, but practically no crystallization occurs; in HCl vapors, together with desulfurization, a very intensive process of crystal growth takes place.

The same proceeds, although to a lesser degree, on calcination in a hydrogen atmosphere, which also leads to the formation of a phosphor. (Hence, the fact that SO_2 itself appears as a desulfurizer becomes clear; SO_2 is, as long known, a good mineralizer for zinc sulfide.)

The calcination of zinc sulfide in dry HCl vapors, although it also brought about no development of azure luminescence, in contrast to the phosphorescence of the normal non-activated zinc sulfide, did on addition of copper produce an intense green Cu-luminescence. The copper was added to the sulfide either before calcination in HCl, or before the subsequent diffusion at 450°. In both instances a brightly luminous ZnSCu-phosphor was obtained. Only the fact that for these preparations the phosphorescence proved to be much weaker than for the ordinary ZnSCu-phosphors was unique.

Having learned that calcination in almost anhydrous HCl vapors was an especially effective desulfurization method, we could expect that in preparations obtained in this way the concentration of [Zn][ ]-centers would be very large. Since we attributed to these centers (non-luminous) the function of acceptors, we expected that we would be able to introduce a great deal of copper into such preparations as green phosphorescence centers. Actually, on introduction of $2 \cdot 10^{-4}$ g of Cu (per 1 g of ZnS) we obtained a phosphor with a purely green phosphorescence (without the least indication of the blue band of copper). By the ordinary methods of preparation of the phosphor, such a large quantity of copper always gives the blue phosphorescence band.

The intensity of the accumulation of free zinc (imparting a gray color to the preparation) on calcination in anhydrous HCl depends on the calcination temperature. The quantity of zinc which accumulated during the preparation was largest at 900° and smallest at 1150°. Here we see a parallelism with the above-described experiments on the thermal decomposition of zinc sulfide in vacuo. A more intense volatilization of zinc occurs at higher temperatures, and less of it remains in the zinc sulfide. Here we again note that it is by no means impossible to simply identify the gray elementary zinc, visible the eye, with the zinc of the [Zn][ ]-centers. The gray color which is visible to the eye, occurred, probably not from the [Zn][ ]-centers themselves, but rather from the colloidal zinc particles which separated at extremely high concentrations of [Zn][ ]-centers in the crystal (or from the zinc in the interstices). Nevertheless, the fact remains that such a macroscopic formation of zinc is a direct demonstration of the occurrence of the decomposition (desulfurization) of the zinc sulfide.

With silver as the activator, we obtained with zinc sulfide calcined in a current of anhydrous HCl results which were entirely analogous to those obtained with copper. Independently of whether silver was added before calcination or before diffusion in the formed preparation, ZnSAg-phosphors with bright phosphorescence were obtained. The situation was very characteristic that here we were able to introduce into the zinc sulfide a larger quantity of silver than by the usual method of preparation of ZnSAg-phosphors. In the ordinary preparation sometimes unintroduced silver remained on the surface of the ZnS-grains, accessible to dissolving in a solution of KCN. Unlike this, the zinc sulfide calcined in dry HCl vapors never gave such a phenomenon. This indicated that the treatment with HCl vapors itself effected the formation of an especially large concentration of [Zn][ ]-centers (acceptors).

Calcination of the zinc sulfide in HCl vapors led to good crystallization of the product. After the first hour of calcination at 1150°, crystals of average size (50 μ) were obtained; moreover, still another observation was made, which we described earlier—the size of the crystals depended on the presence of an activator. If copper was present, then the size of the resulting crystals was considerably larger. The presence of silver also gave this effect, but to a lesser degree.

Conditions of formation of "quenching centers". It has already been mentioned that an extremely weak azure luminescence, not comparable to the phosphorescence of the ordinary non-activated ZnS-phosphor, was obtained by calcination in a current of dry HCl. However, this occurred only with not too strong ultraviolet excitation (i.e., at a weak excitation). By weak excitation we mean, for example, excitation by a lamp of the Osram—Hg QS-300 make at a distance of 40 cm; with such an excitation the product obtained in HCl vapors hardly glows, compared with the ordinary non-activated ZnS-phosphor. If it is excited with intense ultraviolet (advancing the sample directly toward the lamp), then the preparation obtained in HCl vapors glows no less brightly than does the normal non-activated ZnS-phosphor. In other words, for the product obtained in HCl vapors, the dependence of the quantum yield on the

The capacity of the non-activated ZnS-phosphor for azure luminescence depends to a considerable extent on the calcination temperature. The preparations obtained at 800-900° shone most brightly. At higher calcination temperatures the luminescence decreased so that, for example, the preparations calcined at 1250° showed only 0.1 of the maximum brightness. The most simple explanation of this situation is the assumption that the number of [Zn][ ]-centers decreases at sufficiently high temperatures (> 1000°). As a consequence of the decrease of the concentration of the [Zn][ ]-centers, the concentration of the oxygen-containing azure phosphorescence centers must also decrease.* It is possible, however, that the oxygen-containing [O][Zn][ ]-center itself, corresponding to the formula [Zn][S][Zn][O][Zn][ ][Zn][S], at high temperatures, has a tendency toward decomposition, owing to the reaction considered by Guntz [15]:

$$2ZnO + ZnS \rightarrow 3Zn(\uparrow) + SO_2(\uparrow).$$

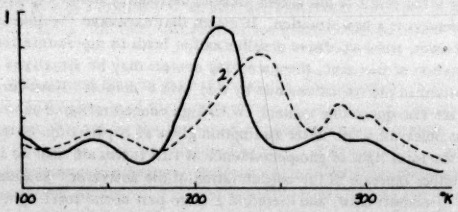

Fig. 6. Thermal absorption curves of two types of ZnSCu-phosphors, excited at 180° by the 336 mμ line.
1) ZnSCu-phosphor containing ZnO; 2) ZnSCu-phosphor containing no ZnO.

Earlier [1] it was shown that this reaction was not observed in macroscopic mixtures of ZnO and ZnS, but in such mixtures there are different energetic conditions than in the oxygen-containing center.

Long ago we observed [3] that the addition of elementary sulfur (of the order of 15%) to the charge during the preparation of ZnSCu-phosphors with above-normal Cu content leads to a considerable intensification of the dark blue portion of the phosphorescence spectrum. This is now completely understood because the addition of sulfur decreases the degree of desulfurization and, consequently, decreases the concentration of the [Zn][ ]-centers. Therefore, the copper was forced to distribute in the least number of acceptors, which also led to the formation of a large number of (Cu)[Cu][ ]-centers of dark blue phosphorescence.

3. Discussion of Literature Data

As the basis of models of the phosphorescence centers we were not only guided by our own experimental material, but also tested the compatability of the models with the experimental results of other authors [15-26]; in addition, we were forced to reproduce and verify the experiments of many authors in order to explain the sources of the experimental contradictions which sometimes arose.

At temperatures of > 1050° Kröger and coworkers [16] tested the effect of the calcination of ZnS-phosphors in different gaseous media (H_2, HCl, H_2S, etc.). Their results were found to be in complete agreement both with the experimental data, and with the models of the center.** From the experiments indicated it may be concluded that, with an increase of the concentration of chlorinating reagents (HCl) in a current of the gas, and with a decrease of the concentration of sulfurizing reagents, the number of Cu-centers of green phosphorescence increases, as compared with the number of Cu-centers of dark blue phosphorescence. This is in complete agreement with the facts presented earlier, from which we may conclude that the more [Zn][ ]-centers form in the zinc sulfide by the action of the chlorinating reagent (and the less the formation of these centers retards the antagonistically-acting sulfurizing reagent), the more acceptors arise in the zinc sulfide, i. e., the more [Cu][ ]-centers of green phosphorescence prevail in them over the (Cu)[Cu][ ]-centers of dark blue phosphorescence.

The interpretation of Kröger and coworkers' results on the repeated calcination of ZnSCu-phosphors in different gases at 400-500° also presented no difficulties. The repeated calcination in HCl vapors brought about an intensification

* At a constant oxygen content.

** Certain obscurities developed even in the evaluation of the results obtained by calcination in HCl; however, we explained these conditions above.

strength of excitation is expressed especially strongly.* Such a sharp dependence of the quantum yield on the strength of excitation indicated the presence of high concentration of "quenching centers". Such a dependence is always shown especially sharply if the ratio $\frac{\text{concentration of phosphorescence centers}}{\text{concentration of quenching centers}}$ is especially low. From the presence of such a sharp dependence we may conclude that in the preparation obtained in dry HCl vapors, there are very few phosphorescence centers and very many quenching centers. The fact that the preparation considered showed a clear red luminescence also indicated the presence of quenching centers. As is known [13], centers with red and infrared radiation act as a quencher with shorter wave, visible emission. The unusually weak phosphorescence, already indicated above, observed on introduction of copper into the product obtained in HCl vapors, is also a characteristic of the presence of a high concentration of quenching centers. (As is known, the phosphorescence is much more sensitive to the presence of "killers" and quenching centers than is the "spontaneous phosphorescence".) The presence of only a small number of azure phosphorescence centers is the result of the known oxygen deficiency in our experiment.** The appearance of a large number of quenching centers is a new situation. It means that excessive desulfurization promotes the formation of quenching centers. Moreover, since excessive desulfurization leads to supersaturation of the crystal by [Zn][ ]-centers and to the formation of free zinc, the quenching centers may be visualized either as associated pairs of [Zn][ ]-centers, or as zinc atoms in the interstices side by side with S-defects. However, it is possible that [Zn][ ]-centers by themselves are also quenching centers. With high concentration of such centers a strong quenching action must occur, which we also observed. The latter assumption gives an explanation of the observation made by Lenard [14], according to which the total light of phosphorescence at first increased with an increasing activator content, but remained constant on further increase of the concentration of the activator. As soon as the activator content is low, many more "free" [Zn][ ]-centers exist, and therefore a large part of the total light of phosphorescence is quenched. The fewer the number of these centers (as a consequence of the replacement of the zinc in them by copper), the weaker the quenching of the total light. When the activator (Cu) occupies all the [Zn][ ]-centers, converting them to [Cu][ ]-centers, no more quenching can occur. However, the independence of the total light of phosphorescence from the activator concentration (at sufficiently high concentrations of the latter) may also be explained by the simple fact that the limitedness of the number of acceptors, i.e., the number of [Zn][ ]-centers in the crystal, also brings on, understandably, a limitedness of the number of the phosphorescing Cu-centers able to develop in the crystal.*** However, it is the limitedness of the number of acceptors able to absorb activator led to simple explanations of the quantitative relation between the total light of phosphorescence and the activator concentration.

In connection with phosphorescence it is worth indicating again that the model of the phosphorescence centers proposed above enables us to understand why, in the ZnS-phosphor, there exists a whole series of different forms of "levels of attachment" (i. e., levels of attachment of different energetic depths). The "temperature curves", having several maxima (Fig. 6) indicated the presence of several different types of levels of attachment in a phosphor. According to our models, one phosphorescence center was a combination of several different anomalous lattices. Take, for example, a Cu-center with a yellowish-green phosphorescence (Fig. 5). There are several different anomalies in it (which can be the source of the singular energetic levels): 1) it lacks an S-ion, 2) a foreign copper atom is present, and 3) one of the S-ions is replaced by an O-ion. Therefore, it is not surprising that in the phosphor there is some "choice" of the different levels of attachment. Moreover, in some ZnS-phosphors there are still free [Zn][ ]-centers and also a considerable quantity of isomorphic inclusions of zinc oxide. It is conspicuous that precisely those ZnSCu phosphors in which there are many isomorphic inclusions of zinc oxide, are characterized by especially long phosphorescence.

* One of us also observed this effect long ago [10] for some common phosphors and, in the meantime, it has been studied in detail by other authors [1, 12]. Earlier [10] it was shown that this effect occurs only at very low temperatures; therefore, we made a comparison of the luminescence of the preparation obtained in HCl vapors with that of the ordinary non-activated ZnS-phosphor at the temperature of liquid air also. At the low temperature the luminosity of the preparation did not differ from that of the ordinary non-activated phosphor, not only with strong, but also with weak excitation. Now it became completely clear why Kröger and Hellingman called the preparation obtained in HCl vapors, "luminous". We turned our attention to the weakness and abnormality of the phosphorescence; Kröger and Hellingman made measurements at −180° C. and at such low temperatures, actually, the difference of the quantum yield from that of the usual non-activated ZnS-phosphor was imperceptible. If we excite at room temperature and, moreover, vary the strength of the excitation, then at once a difference appears between the preparation obtained in HCl vapors and the ordinary non-activated ZnS-phosphor.

** Oxygen (as H_2O) was almost absent in this experiment, but not so completely as in the experiments with the vacuum apparatus [1].

*** Independently of the amount of activator added in the preparation of the phosphor.

of the green phosphorescence band and a weakening of the dark blue band. This corresponds to the facts which we observed. At first glance, it seemed somewhat surprising that repeated calcination at 450° in a current of H_2S brought about an intensification of the green band of copper. However, this becomes understood at once when we consider that at 450° sulfur cannot diffuse inside the crystal but can react only on its surface where it attaches zinc atoms, which at 450° may diffuse freely from the crystal to the surface. These zinc atoms may come also from the interstices and from the zinc in the joints of the lattice. The free joints of the lattice are occupied by copper atoms with the formation of (non-luminous) Cu_2S (or CuS). As a consequence of this, a darkening of the preparation arises, which cannot be removed with a solution of KCN, which was confirmed (experimentally). The impossibility of removing the darkening shows that the Cu_2S actually formed inside the crystals, and not on their surfaces. The copper atoms required for the formation of the Cu_2S were supplied by the (Cu)[Cu][ ]-centers of dark blue phosphorescence, i. e., these centers lose one copper atom and are converted to green phosphorescence centers. Thus, both effects which take place in the repeated calcination of the ZnSCu-phosphor in a H_2S atmosphere at 450° are explained, namely: 1) the darkening, inaccessible to removal by a solution of KCN, and 2) the intensification of the green phosphorescence band at the expense of the dark blue.

Bundel and Rusanova [22] showed that by calcination of the ZnS-phosphors in sulfur vapors they were able in many cases to considerably reduce the brightness of the luminescence. Consequently, this work indicated the essential role of a sulfur deficiency (or excess of zinc) for the formation of phosphorescence centers. True, the authors did not observe the role of oxygen. Moreover, they were limited by the established experimental facts, not considering the special models of phosphorescence centers. Bundel and Rusanova found the greatest quenching effect of the sulfur vapors for non-activated ZnS-phosphor. This was entirely plausible and corresponded to the basic hypotheses of the present work. However, in an experimental respect it proceeds more complexly than appeared on the basis of the data reported by Bundel and Rusanova. We also carried out the experiments described by these authors; the difference consisted of the fact that in [22] non-activated ZnS-phosphor prepared in a nitrogen atmosphere was used, whereas we used non-activated ZnS-phosphor prepared in an atmosphere of air; moreover, different results were obtained. Calcination in sulfur vapors without the addition of a flux to the phosphor, in general, gave no quenching; by the same calcination, in the presence of a flux, we obtained a decrease of the brightness, but it was not comparable to that strong quenching effect which was described in [22].*. Apparently, this divergence of the experimental results was based on the following. As was already mentioned, Bundel and Rusanova prepared their original non-activated ZnS-preparation in a nitrogen atmosphere. As we now know, in the complete absence of oxygen, in general, no luminous non-activated zinc sulfide is obtained [1]. Under the experimental conditions [22] of the complete absence of oxygen it is impossible to expect, certainly, that very little oxygen was present during the preparation of the phosphor.** (This does not mean that, as a consequence of this, the preparations must also have a reduced brightness of luminescence; the brightness of the phosphorescence is by no means proportional to the concentration of the centers, and within wide limits, is almost independent of it). Thus, it becomes understandable why Bundel and Rusanova's preparation underwent quenching by sulfur vapors more readily than did our preparation which contained a much greater concentration of phosphorescence centers.

We carried out experiments on the reaction of sulfur vapors on ZnSCu-phosphors. Bundel and Rusanova reported [22] that these phosphors underwent very little quenching by sulfur vapors. We mention these experiments because they again showed the difference between the oxide-free ZnSCu-phosphors with a purely green phosphorescence and an especially high excitability by α-rays, and the oxygen-containing ZnSCu-phosphors with a yellow-green phosphorescence and an especially long phosphorescence. After high temperature calcination in sulfur vapors (without flux), the former showed no changes, but the latter (after the same calcination) showed a distinct intensification of the dark blue phosphorescence at the expense of the green.

We said above that in the thermal dissociation of non-activated ZnS-phosphor in vacuo, a strong separation of zinc in the phosphor occurs, but no essential weakening of the azure luminescence occurs. In contrast to this, Bundel and Rusanova reported that in the non-activated ZnS-preparation, a strong quenching of the azure luminescence on calcination in vacuo was observed. This discrepancy is again explained by the different concentrations of the centers of phosphorescence. It was stated above that the luminosity is determined by the ratio of the concentration of phosphorescence centers to the concentration of quenching centers. If the concentration of the phosphorescence centers is small, then the quenching effect is strongly expressed, but if the concentrations of the phosphorescence centers is large, then the action of the quenching centers is weakly expressed. This may explain the difference between Bundel and Rusanova's

* At the same sulfur vapor pressures, and other conditions equal.

** Whereas, for all the non-activated ZnS-phosphors prepared in an atmosphere of air, the maximum brightness of luminescence was obtained at calcination temperatures of 800-900°, for the phosphors obtained (continued on next page)

observations and ours.

Gugel [23] found that the addition of Na_2S to the zinc sulfide before the preparation by calcination, caused a considerable change of the properties of the resulting phosphor. For the non-activated zinc sulfide, almost no azure luminescence at all appeared if Na_2S, together with a chloride flux, was present during calcination. In contrast to that, for ZnSCu-phosphors, Na_2S gave no quenching action (down to copper concentrations of the order of 10^{-6} g). The chemical distinction between the phosphors obtained with an without added Na_2S consisted of the fact that, in the first instance, no oxygen from the oxygen-containing, contaminated sulfide ($ZnSO_4$ etc.) remained in the phosphors. In the absence of oxygen, the azure luminescence of the non-activated zinc sulfide was also absent, whereas the copper phosphorescence remained unchanged. As is evident, Gugel's results agree well with our data which was presented earlier [1].

Grillot and Bancie-Grillot [15] found that with almost complete absence of the access of oxygen (and in the presence of a chloride flux) they were unable to obtain a ZnSCu-phosphor with a green phosphorescence; moreover, they obtained only the dark blue copper phosphorescence. It is not difficult to observe that the results [15] are readily amenable to explanation on the basis of our data [1] on the role of oxygen in the action of the flux. With a deficiency of oxygen, the chlorinating and desulfurizing action of the chloride flux is so small that only a low concentration of [Zn][ ]-centers formed, and therefore, on addition of a not too small quantity of copper, only (Cu)[Cu][ ]-centers of dark blue phosphorescence formed.

Grillot, from this experiment and from similar results obtained by Guntz [15], was able to conclude that the presence or absence of oxygen in the center determined whether the center gave green or dark blue phosphorescence. Such an assumption was encountered in the literature [24]. On the basis of these results, it can be assumed that the green phosphorescence center was inherent to the [Cu][O] structure, but the dark blue phosphorescence center was inherent to the [Cu][ ] structure. However, a whole series of facts militates against such hypotheses. The above-described ZnSCu preparation, calcined in HCl vapors, gave only a green band; even on introduction of above-normal quantities of copper the phosphorescence remained green but, nevertheless, this preparation contained almost no oxygen. If the oxygen in the center were responsible for the green phosphorescence then for this preparation only the dark blue band would appear. Still more conclusive is the fact that, on calcination of oxygen-free ZnSCu in hydrogen, we obtained a green phosphorescence, although in this preparation no oxygen could be present. Also the fact may be cited that, on calcination of a ZnSCu-phosphor with a dark blue phosphorescence in a H_2S atmosphere at 450°, the phosphorescence became green.

Smith [25], in his experiments on the effect of oxygen on ZnSAg-phosphors, also investigated the effect of SO_2, considering this gas as an oxygen donor. We also prepared ZnS-phosphors in a current of SO_2 (without use of solid fluxes). Dwelling in no more detail on these experiments, we observe only that this gas acts on the zinc sulfide as a desulfurizer (and gives formation of ZnSCu-phosphor), but its role as an oxygen donor was doubtful, since we were unable to obtain an azure phosphorescence. The desulfurizing action expressed for SO_2 was considerably weaker than for HCl; no visible separation of zinc occurred.

An attempt encountered in the literature [26] to explain the difference between the Cu-centers of the dark blue and the green phosphorescence by the different valence states of copper was also shown to be inadmissible. It was suggested that the dark blue phosphorescence was inherent for monovalent copper, and the green for bivalent copper. The above-described experiment was a direct refutation of this idea, as a result of which the purely green phosphorescence of the ZnSCu-phosphor was obtained by high-temperature calcination in a hydrogen atmosphere (without flux). While Rothschild [26] observed an intensification of the dark blue band of copper, under hydrogen, this was obtained only because the operation was carried out in the presence of a chloride flux at relatively low temperatures, and the hydrogen acted as an oxygen-free inert gas, not promoting the desulfurizing action of the flux. This experiment corresponded to the experiment on production of ZnSCu in an atmosphere of pure oxygen-free nitrogen, where we also obtained the dark blue phosphorescence of copper, for the reasons stated earlier [1].

in [22] in a nitrogen atmosphere this was different; the maximum brightness here was at 1000° but at 800° it was almost 3 times less. This indicates clearly that the preparations had properties which differed from the ordinary. It can be assumed as likely that at higher calcination temperatures more oxygen got into the preparation. Moreover, we recall that at lower temperatures oxygen was also a factor which conditioned the mineralizing action of the flux. With a deficiency of oxygen, and with a low calcination temperature, for example, 800°, the inadequate brightness may also be conditioned by insufficient crystallinity).

SUMMARY

1. On the basis of experiments on the reaction of hydrogen and hydrogen chloride on zinc sulfide phosphors, and on the basis of the results on the role of oxygen obtained in [1], the following model of phosphorescence centers was derived:

a) the azure phosphorescence center was a sulfur defect (excess zinc atom), located side by side with an oxygen ion, replacing one of the neighboring sulfur ions;

b) the sulfur defect by itself (without the presence of oxygen in its vicinity) gave no azure phosphorescence; however, if an excess zinc atom is replaced by a copper atom, then the Cu-center of green phosphorescence is obtained; if still one atom of copper (for example, on one of the adjacent spots in the interstices) is present in the center, then the Cu-center of dark blue phosphorescence is formed;

c) the presence of oxygen is not a necessary condition for the formation of Cu-centers (or for Ag-centers), but its presence in the lattice indicates certain luminescent properties of these centers.

2. The particular effectiveness of chlorinating reagents (HCl or chloride fluxes) is based on their desulfurizing action. Highly luminous ZnSCu-phosphors can also be obtained without a chlorinating reagent, replacing it by another desulfurizing substance, for example, hydrogen. Centers of luminescence formed only if desulfurization occurred simultaneously with the process of crystal growth.

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DITHIOCYANATO-BIS-DIMETHYLGLYOXIME COBALTIACID

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Dinitro-bis-dimethylgloxime cobaltiacid of composition $H[Co(DH)_2(NO_2)_2]\cdot H_2O$ *, apparently the first member of a new series of complex acids $H[Co(DH)_2X_2]$, was obtained by L. A. Tchugeff [1] in 1908. Compounds which include chlorine, bromine [2] and iodine [3] as the acid radicals (X) have been obtained by other investigators. Cambi [4] demonstrated that the dibromo compound bears a genetic relationship to Tchugaeff's acid.

A closer study showed that some difference in the behavior of the dinitro acids and the dihalo compounds exists.

A study of the dithiocyanato derivative was of interest, since it is known from the chemistry of the complex compounds of cobalt that the thiocyanato-group is bound stably by the central atom, and no appreciable tendency toward hydration is shown.

The dithiocyanato compound was obtained on oxidation by the air of a mixture of cobalt salts, dimethylglyoxime and thiocyanate according to the equation:

$$2Co(CH_3COO)_2 + 4DH_2 + 4KSCN + \frac{1}{2}O_2 = 2K[Co(DH)_2(NCS)_2] +$$

$$+ 2CH_3COOK + 2\,CH_3COOH + H_2O,$$

similarly to the production of the diiodo compound [3]. The dithiocyanato-bis-dimethylglyoxime cobaltiacid was precipitated by a strong acid from the dark-brown solution as a reddish-brown, crystalline precipitate of the composition $H[Co(DH)_2(NCS)_2]$.

During the process of oxidation of the mixture a rather large quantity of a dark-brown substance came down. Further investigation showed that this was the very difficultly soluble cobalt salt of the dithiocyanato acid. Its formation decreased the yield of the dithiocyanato acid, since a portion of the dimethylglyoxime remained unreacted.

It proved to be much more convenient to obtain the dithiocyanato acid by the action of a small excess of potassium thiocyanate on the dichloro derivative of cobalt, according to the equation:

$$H[Co(DH)_2Cl_2] + 2KSCN = H[Co(DH)_2(NCS)_2] + 2KCl.$$

The dithiocyanato-bis-dimethylglyoxime cobaltiacid is a strong acid. When water is added to a mixture of the substance and sodium carbonate a frothing occurs as a result of the liberation of CO_2. A determination of the pH of an aqueous solution of this acid also indicated that it is a strong acid.

The following pH values (quinhydrone electrode) were obtained for a 0.001 N aqueous solution of the dithiocyanato acid: shortly after dilution 1.97, and after a day 2.97; calculated for complete dissociation of a monobasic acid at the time of dilution, pH 3.00.

With many cations the dithiocyanato acid gives well-crystallizing salts. They are obtained by the addition of aqueous solutions of the salts to a solution of the acid. It is of interest to record the difficultly-soluble, rose-yellow compound of the composition $Ag\cdot Co(DH)_2(NCS)_2$ which is obtained by the addition of silver nitrate to a solution of the dithiocyanato acid. On trituration of this salt with concentrated hydrochloric acid no formation of silver chloride results. This indicates that silver is bound non-ionically by the SCN group. Such behavior of the thiocyanato-group was noted repeatedly for the cobaltammines. It is certain that also in the acid which we obtained the SCN group was bound by cobalt through nitrogen, as also in all the cobaltammines studied until now.

Thus, the structure of the silver salt can be represented by the formula:

* DH indicates the dimethylglyoxime radical $CH_3-C(=NOH)-C(=NO-)-CH_3$

$$\left[\begin{array}{c}(DH)_2\\ CoNCS\\ NCSAg\end{array}\right]$$

The action of hydroxyl ions on the $[Co(DH)_2(NCS)_2]^-$ anion proved to be very curious. The addition of a small quantity of ammonia to a solution of the dithiocyanato acid in the cold brought about the precipitation of a difficultly-soluble yellow substance of composition $[Co(DH)_2H_2O(NCS)]\cdot H_2O$. This same substance was also formed by the prolonged heating of an aqueous solution of the dithiocyanato acid. An increase of the hydroxyl ion concentration led to the removal of both thiocyanate groups from the complex radical, according to the equation:

$$[Co(DH)_2(NCS)_2]^- + 2OH^- = [Co(DH)_2(OH)_2]^- + 2NCS^-.$$

This reaction enabled us to develop a convenient method of determination of the thiocyanate groups in cobalt thiocyanatodioxime; for this it was sufficient to heat the substance with sodium hydroxide and to add silver nitrate to the solution acidified by nitric acid, so that all of the thiocyanate was precipitated as AgSCN.

The behavior of the dithiocyanato-bis-dimethylglyoxime cobaltiacid with respect to water and hydroxyl ions found its explanation in I. I. Chernyaev's trans-effect rule. As is known, the thiocyanate group was stably bound by the central atom in the cobaltammines [5]. However, for thiocyanatonitrotetrammine cobaltichloride obtained by the action of potassium thiocyanate on chloronitrotetrammine cobaltichloride and which, very likely, has the trans-configuration, Werner and Klien [6] observed considerable increase in time of the electrical conductivity of the aqueous solution. The instability of the bond of the thiocyanato group with cobalt in this compound became evident upon shaking a solution of the salt with silver oxide; at this time a complete breaking away of the thiocyanato group occurred according to the reaction

$$[Co(NH_3)_4(NO_2)(NCS)]Cl + Ag_2O + H_2O = AgCl + AgSCN + \\ + [Co(NH_3)_4(NO_2)(OH)](OH).$$

The trans-effect of the nitro group considerably weakened the bond of the thiocyanato group to cobalt.

One of us found that the trans-effect of the nitro group is considerably intensified by replacement of the four ammonias in $[Co(NH_3)_4(NO_2)_2]^+$ by two DH radicals [7]. By analogy, it was also necessary to attribute to the stable acid radical the more intense trans-effect in the cobalt dioximes. In water or mildly-ammoniacal solution one of the thiocyanato groups weakened the bond of cobalt with the other thiocyanato group, and the latter was replaced by water; in alkali solution the thiocyanato group was replaced by the hydroxyl group, which, having a strong trans-effect, weakened the bond of the second remaining thiocyanato group with cobalt.

The behavior of the dithiocyanato-bis-dimethylglyoxime cobaltiacid which we observed with respect to water and alkali may thus be considered as a new demonstration of the trans-structure of the $[Co(DH)_2X_2]$ radical.

EXPERIMENTAL

Production of Dithiocyanato-bis-Dimethylglyoxime Cobaltiacid

1st Method. 1.2 g of dimethylglyoxime was dissolved in 25 ml of alcohol by slight heating, and a mixture of 1.25 g of $Co(CH_3COO)_2\cdot 4H_2O$ and 1 g of KSCN in 20 ml of water was added to the solution. Air was passed into the resulting dark-brown, clear mixture for 3-4 hours; at this time a certain amount of a dark-brown, almost black precipitate always came down. Concentrated hydrochloric acid was added to the filtrate, a brown color, and at this time the dithiocyanato acid precipitated as fine crystals of a reddish-brown color. The acid yield was ~ 65% of the theoretical. The acid dissolved well in water and in alcohol. It could be recrystallized by dissolving by slight heating in water, followed by precipitation by concentrated nitric or hydrochloric acids.

Analysis of the air-dry substance.

Found %: Co 14.47, 14.47, 14.41, 14.51; SCN 28.44; S 16.04, 15.95; N 20.68. $H[Co(DH)_2(NCS)_2]$. Calculated %: Co 14.51; SCN 28.61; S 15.79; N 20.69.

An analysis of the dark-brown precipitate led to the conclusion that this was nothing else but the salt of the composition $Co[Co(DH)_2(NCS)_2]_2\cdot 2H_2O$.

Found %: Co 19.45, 19.41, 19.33; SCN 25.68, 25.63, 25.38; S 14.18. $Co[Co(DH)_2(NCS)_2]_2\cdot 2H_2O$. Calculated %: Co 19.52; SCN 25.65; S 14.17.

Water was lost only to a negligible extent (0.4% instead of the calculated 3.98%) on heating to 105-110°

In order to demonstrate that the compound was actually the cobalt^{II} dithiocyanato-bis-dimethylglyoxime cobaltiate, the substance was heated with dilute hydrochloric acid (1:1), moreover, the solution had a blue color, and the salt was converted to a finely-crystalline, reddish-brown product.

An analysis of the resulting product showed that this was the dithiocyanato acid.

Found %: Co 14.45; S 15.81. $H[Co(DH_2)(NCS_2]$. Calculated %: Co 14.51; S 15.79.

The conversion of the salt to the thiocyanato acid took place quantitatively.

0.2461 g $Co[Co(DH_2(NCS)_2]_2 \cdot 2H_2O$ gave 0.2091 g $H[Co(DH_2(NCS)_2]$; theoretically it must be 0.2209 g $H[Co(DH_2(NCS)_2]$.

Cobalt was determined in the solution obtained by heating the black salt with hydrochloric acid.

Found %: Co^{II} 6.92, 6.54. $Co^{II}[Co(DH_2(NCS)_2]_2 \cdot 2H_2O$. Calculated %: Co^{II} 6.51.

2nd Method. 1 g of $[CoDH_2DHCl_2]$ was heated with 50-80 ml of water until complete solution. Somewhat more than the calculated quantity of potassium thiocyanate was added to the filtered, greenish-brown solution, whereupon the color of the solution changed to brown. The dithiocyanato acid was precipitated by the addition of concentrated hydrochloric acid. Its yield was ~ 90% of the theoretical.

Found %: Co 14.43; S 15.81. $H[Co(DH_2(NCS)_2]$. Calculated %: Co 14.51; S 15.79.

Dithiocyanato-bis-dimethylglyoxime cobaltiacid gave characteristic precipitates with soluble salts. Finely-crystalline, pale-yellow tetragonal tablets were precipitated by a concentrated solution of LiCl. With a concentrated solution of $FeCl_3$ a brown, microcrystalline precipitate came down. The zinc salt consisted of microscopic rhombohedra almost black with a violet tint. Some of the salts were studied in more detail.

$Cd[Co(DH_2(NCS)_2]_2$ was obtained by precipitation of a solution of the acid by an excess of cadmium nitrate. The precipitate was washed with water, and then with alcohol; it was a finely-crystalline, brown powder.

Analysis of the air-dry substance.

Found %: Co 12.84, 12.77; Cd 12.01; S 13.63. $Cd[Co(DH_2(NCS)_2]_2$. Calculated %: Co 12.77; Cd 12.18; S 13.90.

$Cu[Co(DH_2(NCS)_2]_2 \cdot 2H_2O$ was obtained from solutions of the acid and copper sulfate. It was difficultly soluble in water and in alcohol. It consisted of fine, dark-brown crystals.

Analysis of the air-dry substance.

Found %: Cu 6.86, 6.61, 6.63; Co 13.03, 12.88, 13.05; S 14.27; H_2O 4.63. $Cu[Co(DH_2(NCS)_2]_2 \cdot 2H_2O$. Calculated %: Cu 6.98; Co 12.95; S 14.09; H_2O 3.96.

$Co[Co(DH_2(NCS)_2]_2 \cdot 2H_2O$ was obtained similarly.

Found %: Co 19.44, 19.43; SCN 25.54, 25.81. $Co[Co(DH_2(NCS)_2]_2 \cdot 2H_2O$. Calculated %: Co19.50; SCN 25.65.

This salt was identical with the dithiocyanato acid which formed as a by-product in the first method of production.

$\left[Co(DH_2\begin{matrix}NCS\\NCSAg\end{matrix}\right]$ precipitated at once, by the action of silver nitrate on an aqueous solution of the dithiocyanato acid, as a fine, crystalline rose-yellow precipitate, which was filtered off and washed with water, and then with alcohol. It was insoluble in cold water and in alcohol, and it dissolved with difficulty in hot water.

Analysis of the air-dry substance.

Found %: Ag 20.52, 20.43, 20.30; Co 11.41, 11.29; S 12.14. $\left[Co(DH_2\begin{matrix}NCS\\NCSAg\end{matrix}\right]$. Calculated %: Ag 21.02; Co 11.48; S 12.49.

Silver was stably bound in the complex radical, since the salt, triturated with concentrated hydrochloric acid, gave no silver chloride.

Cobalt Thiocyanato-aquo-bis-dimethylglyoxime

For production of this substance, 1-2 ml of concentrated ammonia was added to a filtered and cooled solution of 1 g of $H[Co(DH_2(NCS)_2]$ in 40 ml of water; a fine, crystalline precipitate of a muddy-yellow color came down at once. The precipitate was washed with water and with alcohol, in which it did not dissolve.

Analysis of air-dry substance.

Found %: Co 15.40, 15.42, 15.41, 15.28; SCN 15.33; S 8.61; H_2O 4.81, 4.65. $[Co(DH)_2H_2O(NCS)]\cdot H_2O$. Calculated %: Co 15.38; SCN 15.16; S 8.37; H_2O 4.70.

On standing in the air the substance, dried at 105°, took up one molecule of water.

Action of water on the dithiocyanato acid. The dithiocyanato acid was entirely stable in aqueous solution, even hot; however, on prolonged heating, the thiocyanato group gradually washed out, and a precipitate of a muddy-yellow color came down. Judging from the results of the analyses, this could be the thiocyanato-aquo-compound, contaminated by the decomposition products of the acid.

Found %: Co 17.57, 18.60, 18.52, 17.85; SCN 13.82; S 10.09, 12.95. $[Co(DH)_2H_2O(NCS)]\cdot H_2O$. Calculated %: Co 15.38; SCN 15.16; S 8.37.

Action of alkali on the dithiocyanato acid. The dithiocyanato acid, heated with a small quantity of sodium hydroxide, gave a clear dark-brown solution. Silver ion precipitated the thiocyanato group quantitatively from the solution acidified with nitric acid.

Found %: SCN 28.53. $H[Co(DH)_2(NCS)_2]$. Calculated %: SCN 28.61.

A study of this reaction showed that in other thiocyanatodioximes heating with alkali also leads to a quantitative splitting-off of the thiocyanato group as SCN^-. This served for the development of a convenient method for the determination of thiocyanogen in the cobalt dioximes.

Method of determination of thiocyanogen in cobalt dioximes. A small quantity of a 7-10% solution of sodium hydroxide was added to a weighed portion of the substance investigated; moreover, the major portion of the substnace dissolved. Then 30-40 ml of water was added, and the mixture was carefully heated until complete dissolution. Dilute nitric acid was added to the cooled alkaline solution until there was a slightly acid reaction and SCN^- precipitated, as usual, as AgSCN.

SUMMARY

1. Dithiocyanato-bis-dimethylglyoxime cobaltiacid.

$$H[Co(DH)_2(NCS)_2]$$

was obtained.

2. The acid gave characteristic salts with many cations. Of them, the salts of Cu, Cd, and Co were studied in detail.

3. By the action of $AgNO_3$ on a solution of the acid, the compound $\left[Co(DH)_2\begin{matrix}NCS\\NCSAg\end{matrix}\right]$ was obtained, in which silver was bound stably in the complex.

4. Cobalt thiocyanato-aquo-bis-dimethylglyoxime $[Co(DH)_2H_2O(NCS)]\cdot H_2O$ was formed by the action of ammonia on the acid.

5. By the action of alkali on the dithiocyanato acid, the thiocyanato groups were quantitatively converted in solution to the SCN^- form. This enabled us to develop a method of determination of the thiocyanato groups in the cobalt dioximes.

6. Proceeding from the trans-effect rule, an explanation of the behavior of the dithiocyanato-bis-dimethylglyoxime cobaltiacid with respect to water and hydroxyl ions was given.

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PROBLEM OF THE DETERMINATION OF THE COMPOSITION OF COMPLEXES BY MULTISTAGE COMPLEX FORMATION

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The determination of the composition of a complex compound, when it appears alone in the system investigated, presents no particular difficulties at the present time. In the event of the simultaneous presence in the solution of several complexes, which differ only in the coordination number, i.e., in the event of multistage complex formation, the complete deciphering of such a system is a much more complicated problem. Its practical solution has very great significance, because multistage complex formation, as is known, is an extremely widespread phenomenon, and in a number of instances has to be considered with the simultaneous existence of two or even three related complexes in the solution.

In K. B. Yatsimirsky's recently published works [1, 2] a method was cited by which the author established the fact of multistage complex formation, the composition and the instability constants of a series of complexes. The essence of this method consists of the following. The system is investigated electrometrically (for example, polarographically) at varying concentrations of the addend. He constructed graphs on the halfwave potential $E_{1/2}$—logarithm of the concentration of the addend (log C) coordinates. If the relationship of these values deviated from linearity, this served as a basis for inferring the presence in a given concentration range of multistage complex formation which, according to the author's assumption, took place according to the scheme:

$$MeX_{p+1} = MeX_p + X.$$

The process then must be described by the equation

$$E_{1/2} = \frac{0.059}{n} \log C^p (C + \kappa) - \frac{0.059}{n} \log K, \qquad (1)$$

where K is the instability constant of the complex with the coordination number p + 1, κ is the constant of the conversion of the complex with a coordination number of p + 1 to the complex with a coordination number of p, and C is the concentration of the addend.

It is easy to see that the graph corresponding to Equation (1) is a smooth curve, turned convexly toward the logarithm-of-C axis. Differentiating Equation (1) with respect to the logarithm of the concentration of the addend, we obtain Equation (2):

$$\frac{\partial E_{1/2}}{\partial \log C} = \frac{0.059}{n} \left(p + \frac{C}{C + \kappa} \right). \qquad (2)$$

At the moment when the concentration of both complexes is equal, i.e., when $C = \kappa$, Equation (2) acquires the following form:

$$\frac{\partial E_{1/2}}{\partial \log C} = \frac{0.059}{n} \left(p + \frac{1}{2} \right). \qquad (3)$$

Giving p the integral values of 1, 2, 3, 4 and 5, the author calculated the value of the angular coefficients from the last equation, and at the calculated angles drew all of the possible tangents to the main curve. In the author's opinion, if n tangents can be drawn, this is a demonstration of the existence of n + 1 complexes. The location of the point of tangency of each tangent enabled the author to calculate the instability constant of each complex from Equation (1).

Analyzing the given method, we concluded that it can lead to erroneous results. As a matter of fact, in his reasoning the author assumes the simultaneous existence of two complexes, which differ in composition by 1 ion (molecule) of the substituent. However, it is known experimentally that during the process of multistage dissociation not 1, but several, for example 2, ions are split off simultaneously.

It can easily be shown that in the event of the splitting off of not one, but q substituents, Expressions (1) and (2) are transformed, respectively:

$$E_{1/2} = \frac{0.059}{n} \log C^p (C^q + \kappa) - \frac{0.059}{n} \log K \qquad (4)$$

and

$$\frac{\partial E_{1/2}}{\partial \log C} = \frac{0.059}{n} \left(p + \frac{q \cdot C^q}{C^q + \kappa} \right). \qquad (5)$$

An analysis of these expressions showed that also in this general case, as for $q = 1$, the relationship of $E_{1/2}$ – –log C is represented by a smooth curve turned convexly toward the log C axis. With changes of the ratio between κ and C^q from $\kappa > C^q$ to $\kappa < C^q$ the angular coefficient changes smoothly from $\frac{0.059}{n} p$ to $\frac{0.059}{n} (p + q)$.

Therefore, if any coordination number between the actually existing numbers p and p + q is impossible, for spatial or any other reasons, it can be derived just the same by Yatsimirsky's method, since the tangent at the corresponding angle can be drawn. Proceeding from the position of this tangent, we can even calculate the instability constant for such a non-existent complex compound.

But before the appearance of the cited works of K. B. Yatsimirsky, some investigators arrived at a solution of the problem from the same positions. Thus, Korshunov and Malyugina [3], investigating the interaction of copper salts with pyridine polarographically, and obtaining a smooth curve of the $E_{1/2}$ –log C relationship, calculated on the basis of this curve the instability constants for complex compounds with coordination numbers of 2, 3, 4 and 6. The authors omitted the complex compound with the coordination number of 5, probably assuming such a coordination number as unreal. However, from the point of view of the method discussed, such a coordination number is equal with all the rest. In another work [4] the same smooth curves gave the authors a basis for calculating the instability constants for the halide complexes of cadmium with coordination numbers of 1, 2, 3, 4 and 6.

In our opinion, the analysis of the $E_{1/2}$ –log C relationship can lead only to a demonstration of the existence of complex compounds with a definite coordination number, when on the $E_{1/2}$ –log C curve a considerable linear region is observed (corresponding, for example, to a change of log C by 2 units). In this instance the calculation of the constants is legitimate. In the absence of such regions, apparently, we can use only the initial and final positions of the tangents to the curve in the calculation, i.e., the minimum and maximum coordination numbers possible for a given concentration range. In this circumstance, intermediate compositions can be neither demonstrated nor confirmed by such a method. The use of the curve for the calculation of instability constants is possible only for those complexes the existence of which was reliably established by some independent method.

In the literature there are many examples of the fact that, for similar types of investigations, the specified linear regions are actually obtained quite often. It is possible, for example, to mention the work of Stackelberg and Freyhold [5], who, investigating the composition of cuprammonium complexes polarographically, obtained for $[Cu(NH_3)_4]^{2+}$ and $[Cu(NH_3)_2]^{+}$ significant linear regions on the $E_{1/2}$ – log C curves.

V. F. Toropova and F. M. Batyrshina [6] obtained linear regions corresponding to $Pb(CH_3COO)^{+}$ and $[Pb(CH_3COO)_4]^{2+}$ for the acetate complexes of lead.

These data inspire confidence. However, the authors found it possible to infer the existence of the $[Pb(CH_3COO)_3]^{-}$ ion from the curved region of the graph, although with the same degree of probability it could have indicated the existence of a complex with a coordination number equal to two, about which the authors said nothing. With certainty this results from a consideration of the figures which they cited in Table 1.

The same linear region was obtained by O. S. Fedorova [7] for the thiourea complexes of cadmium and lead, and also by A. M. Vasilyev and V. I. Proukhina [8] for a series of halide complexes of the same metals. It is impossible to object to the composition of the complexes found by such a principle.

All the consideration which we have expressed refer entirely to the solution of the problem of the composition of complex compounds by means of the potentiometric method [2], which in its essence and also in its form is entirely analogous to the polarographic method considered.

Works in which unfounded conclusions were drawn on the basis of such potentiometric investigations were encountered in the literature. Thus, Toropova [9], obtaining a curvilinear relationship of the potential and the logarithm

of the concentration of thiosulfate-ion, and drawing two tangents to this curve, wrote in the summary: "It was shown that . . . Hg^{2+} formed with $S_2O_3^{2-}$ ions the complexes: $[Hg(S_2O_3)_2]^{2-}$ and $[Hg(S_2O_3)_3]^{4-}$ and $[Hg(S_2O_3)_4]^{6-}$". Actually, these data enabled Toropova to confirm the existence of the $[Hg(S_2O_3)_4]^{6-}$ ion, to assume the presence of the $[Hg(S_2O_3)_2]^{2-}$-ion, but not to refer to the $[Hg(S_2O_3)_3]^{4-}$ ion.

It should be noted that in the above-cited work of Yatsimirsky [2], on the presentation of a method of determination of the composition of complex compounds from the solubility, the possibility of multistage complex formation by addition of not one, but several addends at once, was indicated. Nevertheless, he overlooked this correct position for some reason or other, For example, considering the interaction of Cd^{2+} with NH_3 [1], the author, observing 2 points of tangency to the curve, wrote: "...In the solution, consequently, ...exist the complex ions $[Cd(NH_3)_3]^{2+}$, $[Cd(NH_3)_4]^{2+}$, and $[Cd(NH_3)_5]^{2+}$".

In conclusion we want to emphasize thoroughly the picture of the complexity of a complete solution of this problem; we stated its considerations in connection with the fact that, as was shown, the method considered may lead to unfounded and, possibly, erroneous conclusions.

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ELECTRICAL CONDUCTIVITY, VISCOSITY AND DENSITY OF THE SYSTEM $SnBr_4 - CH_3COOH$

M. Usanovich and E. Yakovleva

Stranathen and Strong [1] studied the electrical conductivity and viscosity of the system $SnCl_4 - CH_3COOH$ and deduced the existence of the compound $SnCl_4 \cdot 3CH_3COOH$. M. Usanovich and E. Kalabanovskaya [2, 3], assuming that, together with the compound $SnCl_4 \cdot 3CH_3COOH$, the compound $SnCl_4 \cdot 2CH_3COOH$ must exist, repeated the viscosity and electrical conductivity measurements in a wider temperature range. However, no specific points corresponding to the compound $SnCl_4 \cdot 2CH_3COOH$ were produced on the curves. Continuing to assume that the compound $SnCl_4 \cdot 2CH_3COOH$ must exist, the authors attempted to isolate it in the crystalline state. And actually, a compound $SnCl_4 \cdot 2CH_3COOH$ with a m. p. of 19.5° was isolated.

In connection with these data, it was of interest to study the behavior of $SnBr_4$ with respect to CH_3COOH. For this purpose the electrical conductivity, viscosity and density of the system $SnBr_4 - CH_3COOH$ were studied.

The acetic acid and the stannic bromide were carefully purified and their constants corresponded to the literature values. Measurements of the electrical conductivity, viscosity and density were made at 25, 60 and 70°.

Stannic bromide, like stannic chloride, mixed limitedly with acetic acid. In the system $SnCl_4 - CH_3COOH$ separation set in at 40 mole % of $SnCl_4$ at 0°, but in the system $SnBr_4 - CH_3COOH$ at 25° the region of separation lay between 70-20 mole % of $SnBr_4$. Stannic bromide mixed in all proportions with acetic acid at 60 and 75°; therefore, incomplete curves were obtained at 25°.

The results of the measurement of the viscosity, electrical conductivity and density are given in Figs. 1, 2 and 3, respectively. On addition of acetic acid to the stannic bromide, the viscosity of the latter decreased a little at first. A further increase of the acetic acid concentration led to a viscosity increase. This viscosity increase was very sharply expressed at 25°. The viscosity isotherms passed through a maximum which occurred at ~ 15-20 mole % $SnBr_4$. With an increase of the temperature, the viscosity of the system decreased strongly, especially in the region of the maximum. While the viscosity isotherm at 25° passed through a sharp maximum, on the viscosity isotherm at 75° the maximum was weakly expressed.

Such a course of the viscosity isotherms, on the one hand, indicates that interaction occurs in the system, and on the other, shows that the compound which forms is apparently thermally unstable.

The specific electrical conductivity isotherms (Fig. 2), which pass through a maximum at 10 mole % $SnBr_4$, also indicated the presence of interaction. It is interesting to observe the unusual relationship of the electrical conductivity of the system to the temperature. The electrical conductivity isotherm at 75° was located between the 25 and 60° isotherms. Such a position of the electrical conductivity isotherm was related to the change of the viscosity with temperature. It is obvious from Fig. 1 that the viscosity at 25° in the region of the maximum is approximately 5 times larger than that at 60°, but the viscosity at 75° differs relatively little from that at 60°; therefore, if a correction is made for viscosity, the electrical conductivity isotherms are arranged regularly (Fig. 4). The corrected electrical conductivity decreases sharply with an increase of temperature which, in our opinion, also indicates the thermal instability of the complex compounds which form in the system.

The study of the system $SnBr_4 - CH_3COOH$ showed that $SnBr_4$ differed from stannic chloride in its behavior. It was established by the works of many investigators that $SnBr_4$ had much less of a tendency toward formation of complex compounds than did $SnCl_4$. The compounds of $SnBr_4$ were less stable than were the corresponding compounds of $SnCl_4$. It is evident from the data cited that stannic bromide reacts with acetic acid; the presence of electrical conductivity in the system shows that this reaction is of an acid-base nature. However, the curves of the physico-chemical analysis of the liquid phase gave no indication of the composition of the complex compounds which formed in the system.

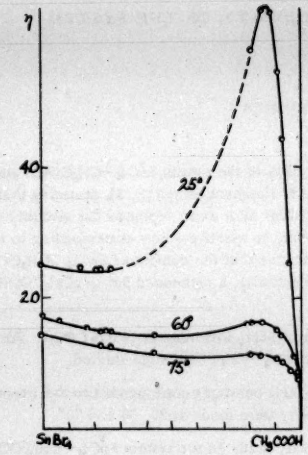

Fig. 1. Viscosity of the system $SnBr_4 - CH_3COOH$ (in centipoises).

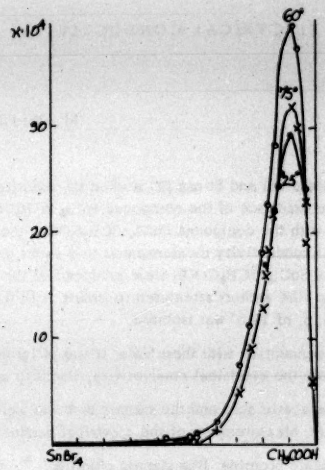

Fig. 2. Specific electrical conductivity of the system $SnBr_4 - CH_3COOH$.

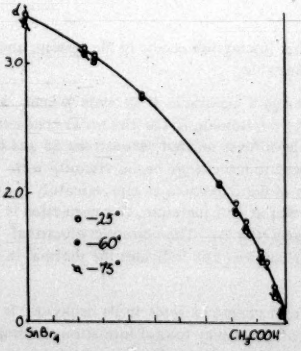

Fig. 3. Density of the system $SnBr_4 - CH_3COOH$.

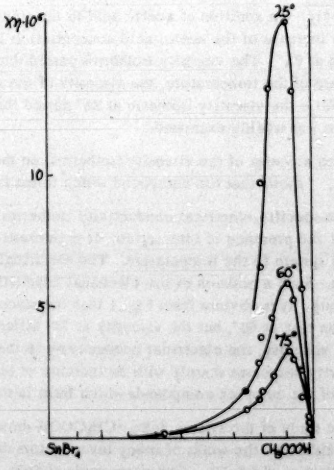

Fig. 4. Corrected electrical conductivity of the system $SnBr_4 - CH_3COOH$.

SUMMARY

1. The electrical conductivity, viscosity and density of the system $SnBr_4-CH_3COOH$ were studied at 25, 60 and 75°.

2. By the curves of the physico-chemical analysis of the liquid phase, it was established that stannic bromide reacts with acetic acid. The presence of electrical conductivity in the system showed that this interaction was of an acid-base nature.

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VISCOSITY OF THE THREE-COMPONENT SYSTEM n-HEPTANE – n-OCTANE – 2,2,4-TRIMETHYLPENTANE

A. P. Toropov, R. P. Airapetova and V. K. Kiryukhin

The refined formula, proposed by G. M. Panchenkov [1], for the calculation of the viscosity of liquids was verified by the author for individual substances. The verification of the applicability of the new formula to the calculation of the viscosity of mixtures was of definite interest, as part of the general problem of a detailed verification of the theory of the viscosity of liquids developed by Panchenkov. In particular, the calculation of the viscosity of a three-component system enabled us to check the validity of some results from the ideas evolved by the author.

In the literature we were unable to find data on the viscosity of three-component systems, suitable for calculations by the Panchenkov formula. The majority of the three-component systems were studied at only one temperature [2]. We knew of only one three-component system, studied at two temperatures [3], but this system was inconvenient for the calculations, since it was singular, and at iso-concentrations a rather strong dispersion of the points was observed; moreover, it was studied in a narrow temperature range; therefore, we studied it for the viscosity of the three-component system, n-heptane -n-octane -2, 2, 4-trimethylpentane. The choice of components was conditioned by the desire, together with the problems posed above, to follow also the relationship of the bond energy of the mixture to the composition, studied by one of us [4] for the formation of ideal solutions, which occurs in this system.

The substances were purified by fractional distillation, by which fractions boiling at a strictly constant temperature were selected; the resulting preparations were characterized by the viscosity and density values cited in the tables below. The viscosity was measured in a capillary viscosimeter for highly volatile liquids [5], which had a discharge time of 102.4 seconds for water at 20°. The discharge time was measured with an accuracy of $\pm$ 0.2 second. The density was determined in a pycnometer for a volume of about 1 ml. The measurements were made at 20, 40 and 60°, maintaining an accuracy of $\pm$ 0.02°. For calculation of the viscosity, the expansion of the liquid in the viscosimeter with an increase of temperature was taken into account [6]. A calculation of the correction for the kinetic energy, according to Barr [6], showed that for the substances enumerated above this correction was much smaller than the experimental error; therefore, no correction for the kinetic energy was introduced for the viscosity calculations.

The interpolated results of the measurements for binary systems are cited in Tables 1, 2 and 3 (the designations used are the same as in Panchenkov's works; ϵ_C and ϵ_{12} are given in calories per mole). The results of the viscosity and bond energy calculations are cited in the same tables, wherein the values of ϵ_{12} are calculated for all the component ratios cited, rather than for any one ratio, as Panchenkov recommended [7]. This was done in order to obtain the most reliable average value of ϵ_{12}. The value of log A_S at 20° was calculated.

As is evident from Tables 1, 2 and 3 the discrepancy between the experimental values of the viscosity and the values calculated from Panchenkov's refined formula [1], in no case exceeded the experimental error, which indicates the sound applicability of this formula to the calculation of the viscosity of mixtures for the binary systems studied. On the bond energy-composition curves, which one of us proposed [4], a linear relationship of the bond energy to the composition expressed in mole fractions, was observed. Curves of this form were observed for the first time.

Further, we measured at the same temperatures as for the binary systems, the viscosities of six ternary mixtures of the components of the system studied. The bond energies of the mixture were calculated from the viscosity and density values for these mixtures. According to the ideas evolved by Panchenkov [7], the bond energy for the three-component mixture may be calculated, if the bond energy values of the pure components and the bond energy of the components with each other in pairs are known. Designating the components of the ternary system by the indices 1, 2 and 3, we obtained the following expression (C is the mole fraction) after a simple calculation:

$$\epsilon_C = \epsilon_{11}C_1^2 + \epsilon_{22}C_2^2 + \epsilon_{33}C_3^2 + 2\epsilon_{12}C_1C_2 + 2\epsilon_{13}C_1C_3 + 2\epsilon_{23}C_2C_3.$$

Using this expression, we calculated the bond energy values for the ternary mixtures which we used, using for ϵ_{12}, ϵ_{13} and ϵ_{23} their average values. The results of the calculations by two methods are cited in Table 4.

TABLE 1

n-Heptane–n-Octane

n-C_7H_{16} (in mole %)	20°		40°			60°			log A_S	ϵ_C	ϵ_{12}
	$\eta \cdot 10^3$	d_4^{20}	$\eta \cdot 10^3$	$\eta \cdot 10^3$, according to Panchenkov	d_4^{40}	$\eta \cdot 10^3$	$\eta \cdot 10^3$ according to Panchenkov	d_4^{60}			
0.0	5.39	0.7031	4.29	4.28	0.6869	3.48	3.48	0.6703	$\bar{5}$.1936	2041	–
20.0	5.11	0.6991	4.07	4.08	0.6824	3.33	3.33	0.6658	$\bar{5}$.2176	1984	1898
40.0	4.84	0.6954	3.87	3.88	0.6788	3.18	3.18	0.6618	$\bar{5}$.2399	1928	1899
60.0	4.58	0.6919	3.68	3.69	0.6751	3.04	3.04	0.6579	$\bar{5}$.2549	1882	1921
80.0	4.33	0.6886	3.50	3.51	0.6716	2.90	2.90	0.6543	$\bar{5}$.2753	1828	1938
100.0	4.08	0.6855	3.32	3.33	0.6686	2.76	2.76	0.6511	$\bar{5}$.3052	1760	–

TABLE 2

n-Heptane–2,2,4-Trimethylpentane

iso-C_8H_{18} (in mole %)	20°		40°			60°			log A_S	ϵ_C	ϵ_{23}
	$\eta \cdot 10^3$	d_4^{20}	$\eta \cdot 10^3$	$\eta \cdot 10^3$, according to Panchenkov	d_4^{40}	$\eta \cdot 10^3$	$\eta \cdot 10^3$ according to Panchenkov	d_4^{60}			
0.0	4.08	0.6855	3.32	3.33	0.6686	2.76	2.76	0.6511	$\bar{5}$.3052	1760	–
20.0	4.23	0.6877	3.43	3.42	0.6709	2.84	2.83	0.6534	$\bar{5}$.2758	1814	1907
40.0	4.38	0.6899	3.54	3.54	0.6731	2.92	2.92	0.6557	$\bar{5}$.2652	1846	1881
60.0	4.54	0.6919	3.66	3.67	0.6751	3.02	3.02	0.6578	$\bar{5}$.2620	1868	1854
80.0	4.73	0.6935	3.80	3.81	0.6771	3.13	3.13	0.6598	$\bar{5}$.2563	1896	1835
100.0	4.98	0.6956	3.98	4.00	0.6789	3.27	3.27	0.6618	$\bar{5}$.2471	1935	–

TABLE 3

n-Octane–2,2,4-Trimethylpentane

iso-C_8H_{18} (in mole %)	20°		40°			60°			log A_S	ϵ_C	ϵ_{13}
	$\eta \cdot 10^3$	d_4^{20}	$\eta \cdot 10^3$	$\eta \cdot 10^3$, according to Panchenkov	d_4^{40}	$\eta \cdot 10^3$	$\eta \cdot 10^3$ according to Panchenkov	d_4^{60}			
0.0	5.39	0.7031	4.29	4.28	0.6869	3.48	3.48	0.6703	$\bar{5}$.1936	2041	–
20.0	5.28	0.7017	4.21	4.21	0.6856	3.43	3.43	0.6689	$\bar{5}$.2119	2007	1948
40.0	5.19	0.7003	4.15	4.14	0.6841	3.38	3.38	0.6674	$\bar{5}$.2144	1995	1981
60.0	5.10	0.6988	4.08	4.08	0.6825	3.34	3.34	0.6657	$\bar{5}$.2301	1967	1966
80.0	5.03	0.6972	4.03	4.04	0.6808	3.31	3.31	0.6638	$\bar{5}$.2486	1937	1928
100.0	4.98	0.6956	3.98	4.00	0.6789	3.27	3.27	0.6618	$\bar{5}$.2471	1935	–

TABLE 4

n-Heptane–n-Octane–2,2,4-Trimethylpentane

Mixtures	Composition of mixture (in mole %)			ϵ_C, calculated from viscosity of ternary mixtures	ϵ_C, calculated from bond energies for binary systems	Deviations (in %)
	n-C_8H_{18}	n-C_7H_{16}	2,2,4-trimethylpentane			
I	19.61	60.09	20.30	1856	1857	0.0
II	39.47	40.47	20.06	1932	1909	– 1.2
III	19.98	40.10	39.92	1915	1893	– 1.2
IV	59.68	20.12	20.20	1987	1964	– 1.2
V	39.45	20.72	39.83	1903	1936	+ 1.7
VI	19.01	19.47	61.52	1904	1920	+ 0.8

TABLE 5

n-Heptane–n-Octane–2,2,4-Trimethylpentane

Mixtures	20°		40°				60°				log A_S
	$\eta \cdot 10^3$	d_4^{20}	$\eta \cdot 10^3$	$\eta \cdot 10^3$, according to Panchenkov	$\Delta\eta$ (%)	d_4^{40}	$\eta \cdot 10^3$	$\eta \cdot 10^3$, according to Panchenkov	$\Delta\eta$ (%)	d_4^{60}	
I	4.54	0.6925	3.69	3.67	−0.5	0.6755	3.03	3.03	0.0	0.6595	$\bar{5}.2702$
II	4.77	0.6938	3.89	3.85	−1.0	0.6796	3.15	3.16	+0.3	0.6622	$\bar{5}.2497$
III	4.73	0.6935	3.81	3.81	0.0	0.6772	3.11	3.12	+0.3	0.6587	$\bar{5}.2587$
IV	5.04	0.6987	4.07	4.03	−1.0	0.6820	3.29	3.30	+0.3	0.6662	$\bar{5}.2272$
V	4.91	0.6954	3.98	3.96	−0.5	0.6803	3.27	3.25	−0.6	0.6640	$\bar{5}.2414$
VI	4.87	0.6944	3.92	3.92	0.0	0.6777	3.22	3.21	−0.3	0.6601	$\bar{5}.2503$

As may be seen, the correspondence of the bond energy values of the mixtures, obtained by two independent methods, is satisfactory, which favors the use of the above-mentioned ideas of Panchenkov.

The results of the viscosity and density measurements of ternary mixtures and the viscosity values calculated according to Panchenkov are cited in Table 5. For the calculations we used the bond energy values of the mixture, calculated from the bond energies for the binary systems, i.e., obtained not from experimental data, but by an indirect method.

As is evident from the data of Table 5, the correspondence of the experimentally obtained viscosity values and the calculated viscosity values is satisfactory.

SUMMARY

1. The viscosity and density of the system, n-heptane–n-octane–2,2,4-trimethylpentane, were studied at 20, 40 and 60°.

2. The applicability of Panchenkov's refined formula to the calculation of the viscosity of the system was shown.

3. The feasibility of the calculation of the bond energy of the ternary mixture from data for binary systems was shown.

4. In the individual binary systems of n-heptane–n-octane, n-heptane–2,2,4-trimethylpentane, and n-octane–2,2,4-trimethylpentane the relation of the bond energy of the mixture to the composition, expressed in mole fractions, was linear.

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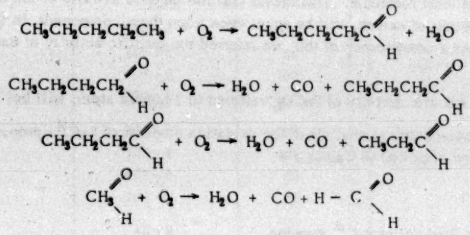
THEORY OF THE DESTRUCTIVE OXIDATION OF HYDROCARBONS

M. B. Neiman, A. F. Lukovnikov and G. I. Feklisov

The theory of destructive oxidation, introduced in 1929 by American chemists [1] attained wide circulation in the interpretation of the mechanism of the oxidation of hydrocarbons. According to this theory the hydrocarbon molecule begins to oxidize at the end carbon of the chain and gradually decomposes in proportion to the oxidation, splitting off carbon monoxide and water. Thus, for example, the scheme of destructive oxidation of pentane will appear as follows:



In a series of works, S. S. Nametkin [2] propagated the theory of destructive oxidation. As a basis of this theory, Norrish drew on much experimental material obtained by the application of various new methods of physico-chemical analysis. This theory correctly reflects some experimental facts, especially the presence of a series of lower and higher aldehydes in the oxidation products. The presence of different aldehydes is shown especially clearly in one of Norrish's recent works on an investigation of the oxidation of hexane [3].

However, reflecting the formation of aldehydes, water and carbon monoxide, the theory did not at all show methods by which the alcohols, peroxides and less complex hydrocarbons, among them the olefins and a series of other products, were formed by the oxidation of hydrocarbons.

This condition induced us to carry out work on the verification of the correctness of the theory of destructive oxidation; moreover, we used the method of tagged atoms.

From a consideration of the scheme of destructive oxidation it is evident that, in the event of the correctness of the theory, formaldehyde can form only from the end, and acetaldehyde only from the two side carbon atoms of the molecule which is oxidized. Precisely these positions also were investigated experimentally. In order to establish what atoms of the hydrocarbon molecules formed the formaldehyde and acetaldehyde, 2-C^{14}-propane, n-1-C^{14}-butane, n-1-C^{14}-pentane and n-3-C^{14}-pentane were synthesized.

2-C^{14}-Propane was prepared from tagged isopropyl alcohol via the organomagnesium compound. The preparation of the isopropyl alcohol, and of the isotopic isomers of butane and pentane was described earlier [4-6].

Tagged C^{14}-butane and pentane were subjected to oxidation by molecular oxygen at 305° and at a pressure of the gaseous mixture of 200-220 mm, in a glass vessel under static conditions. Under the conditions which we chose the process of the oxidation of butane and pentane was accompanied by the blazing up of a cold flame. The reaction products were removed both directly before the blazing up of the cold flame, and also after the blazing up.

2-C^{14}-Propane was oxidized by the oxygen of the air at 340° and atmospheric pressure in a glass vessel under flow conditions. The contact time amounted to 18.2 seconds. Under these conditions about 50% of the propane was oxidized. From the oxidation products the most diverse compounds were isolated, among them formaldehyde and acetaldehyde as the dimedon derivatives, and also CO and CO_2 as $BaCO_3$. After purification and recrystallization the dimedonates of the aldehydes and the samples of $BaCO_3$ were subjected to radiometric investigation.

On calculation of the specific activity of the measured compounds we introduced a correction for the absorption of β-radiation of the C^{14} in the thickness of the measured sample. The calculation was made by the equation:

$$I = \frac{a}{\mu}(1-e^{\mu x}),$$

where I is the measured radioactivity (in counts/min.), a is the specific activity (in counts/min · mg), x is the thickness of the layer of the measured sample (in mg/cm²), and μ is the coefficient of self-absorption (in cm²/mg).

The value of μ which we found by the experimental method amounted to 0.294 cm²/mg. As a consequence of the fact that the compounds of different chemical composition were subjected to radiochemical measurement, the determined values of the specific activities were converted to the standard compound, as which $BaCO_3$ was used; moreover, we used the formula: $\alpha' = \alpha \frac{M_{compd.}}{n \cdot 197.4}$, where α is the specific activity of the measured compound, α' is its value converted to $BaCO_3$, n is the number of carbon atoms in the molecule of the measured compound, and $M_{compd.}$ is the molecular weight of the measured compound. All of the initial tagged hydrocarbons and their oxidation products had only 1 tagged atom in their molecule. This meant that the specific activity of the $BaCO_3$ samples obtained from compounds with 1 and n atoms of carbon, will be equal even when these compounds, in the quantity of 1 mole, will have the same activity. As a consequence of this, we referred the specific activity of $BaCO_3$ to one tagged atom of the compound.

In this instance the specific activity of $BaCO_3$, referred to 1 tagged atom, will be: $\alpha'' = \alpha'_1 = \alpha \frac{M_{compd.}}{197.4}$.

The results of the radiochemical analysis of the oxidation products of 2-C^{14}- propane, 1-C^{14}-butane, 1-C^{14}-pentane and 3-C^{14}- pentane are cited in Tables 1-4.

TABLE 1

Radioactivity of Oxidation Products of 2-C^{14}-Propane
(Oxidation was carried out in a current at 340°; the contact time was 18.2 seconds).

Products	Weight of sample (mg).	Activity (counts/min.)	Specific activity		
			compounds	for 1 atom	relative (%)
C_3H_8 original	6.1	176±3	76	228	
	4.0	124±4	70	219	100
CO_2	8.5	236±5	88	88	52
	12.0	275±5	88		
CH_2O	18.2	86±2	26	38.5	22.6
	21.2	85±2	25.5		
	32.9	90±3	26		
	34.0	90±3	26		
CH_3CHO	16.4	373±5	115	170	100
	17.4	384±5	117		
CO	8.7	104±3	38	38	22
	8.9	105±3	37.5		

The relative activity value of the reaction product studied is cited in the last column of each of the tables, for tagged atoms of the original hydrocarbon, converted to the reaction product.

It is clearly evident from the above-cited data of the tables that formaldehyde, acetaldehyde, CO and CO_2 formed from different parts of the carbon chain of the hydrocarbon; therefore, any carbon atom of the original molecule can participate in the formation of the carbon skeleton of the aldehyde.

We used the relative specific activity of the formaldehyde and acetaldehyde which formed on oxidation of the hydrocarbons tagged with radio carbon in different parts of the carbon chain for the calculation of the probabilities of formation of these compounds from different carbon atoms of the original molecule.

TABLE 2

Radioactivity of Oxidation Products of 1-C^{14}-Butane

(Temperature 306°; initial pressure 220 mm; products were removed after passage of the cold flame)

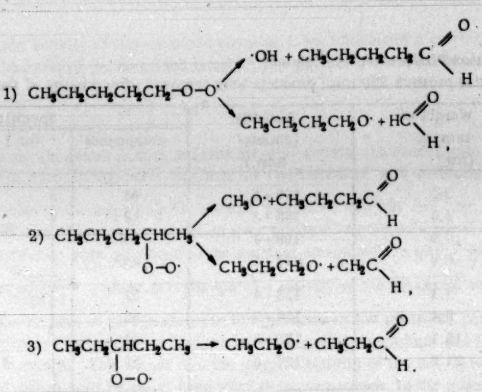
Products	Weight of sample (mg)	Activity (counts/min.)	Specific activity		
			compounds	for 1 atom	relative (%)
C_4H_{10} (original)	3.3	142 ± 5	90	354	100
	4.0	143 ± 3	88		
	5.9	198 ± 4	87		
	6.4	213 ± 5	89		
CH_2O	7.1	128 ± 4	52	79	22
	9.4	150 ± 3	53		
	15.1	175 ± 5	54		
	21.6	187 ± 5	54		
CH_3CHO	8.7	270 ± 6	100	144	41
	10.6	265 ± 6	90		
	12.4	296 ± 6	100		
	15.9	320 ± 6	100		
CO	5.5	138 ± 5	64	66	18.5
	7.9	170 ± 5	66		
	9.2	188 ± 5	68		
	11.3	209 ± 5	68		
CO_2	2.4	48 ± 2	38	40	11
	3.0	59 ± 2	40		
	3.7	68 ± 2	40		
	5.8	99 ± 2	44		

TABLE 3

Radioactivity of Oxidation Products of 1-C^{14}-Pentane

(Temperature 305°, initial pressure 195 mm; induction period of cold flame 5.6 seconds, products were removed after 60 seconds).

Products	Weight of sample (mg)	Activity (counts/min.)	Specific activity		
			compounds	for 1 atom	relative (%)
C_5H_{12} (original)	3.3	136 ± 4	87	400	100
	7.3	206 ± 3	81		
	11.4	219 ± 2	72		
	21.9	234 ± 3	70		
CH_2O	8.1	136 ± 5	51	77	17
	11.1	148 ± 5	49		
	19.8	186 ± 5	56		
	25.1	186 ± 3	54		
CH_3CHO	3.3	192 ± 3	120	170	43
	6.2	279 ± 2	120		
	9.4	310 ± 2	110		
	38.6	395 ± 2	110		
CO	3.8	90 ± 3	53	51	13
	4.9	105 ± 5	52		
	5.3	102 ± 5	48		
	6.1	122 ± 5	53		
CO_2	5.7	90 ± 3	40	47	12
	6.8	127 ± 6	52		
	7.9	128 ± 6	49		
	14.14	154 ± 7	48		



This radical-chain oxidation mechanism, substantiated by Semenov, thoroughly explains the presence in the oxidation products of all sizes of aldehydes which are formed, by taking account of the different radicals present in the oxidation chain.

For an explanation of the feasibility of the formation of formaldehyde from all the carbon atoms of the chain of the oxidized molecule which we discovered, we assume it necessary to supplement this scheme by decomposition reactions of the alcohol radicals. In our opinion, the alcohol radicals not only can add hydrogen, with the formation of alcohol molecules, but are also decomposed, with the formation of formaldehyde, by the reaction:

$$RCH_2O^{\cdot} \longrightarrow R^{\cdot} + CH_2O.$$

This decomposition was almost thermoneutral and, in any case, involved no large negative heat effect. We assumed that the relative probability of this reaction increased in proportion to the complexity of the R radical. Such an assumption explains the feasibility of the formation of formaldehyde from all the carbon atoms of the hydrocarbon, and also enables us to understand why considerable quantities of the lower alcohols can be observed in the oxidation products of complex hydrocarbons.

SUMMARY

1. A radiometric investigation of the oxidation products of propane, butane and pentane, tagged with C^{14} showed that formaldehyde and acetaldehyde formed from different parts of the carbon chain, and not only from its end atoms as the theory of destructive oxidation of hydrocarbons maintained.

2. The experimental data are best explained by N. N. Semenov's radical-chain scheme. This scheme should be supplemented by the decomposition reactions of the alcohol radicals $RCH_2O^{\cdot} \longrightarrow R^{\cdot} + CH_2O$, explaining the feasibility of the formation of formaldehyde from all of the C-atoms of the carbon chain.

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ISOMERIC TRANSFORMATIONS OF ACETYLENE HALIDES IN THE ORGANO-ELEMENTARY SYNTHESIS OF ALCOHOLS

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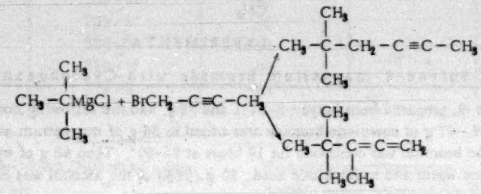
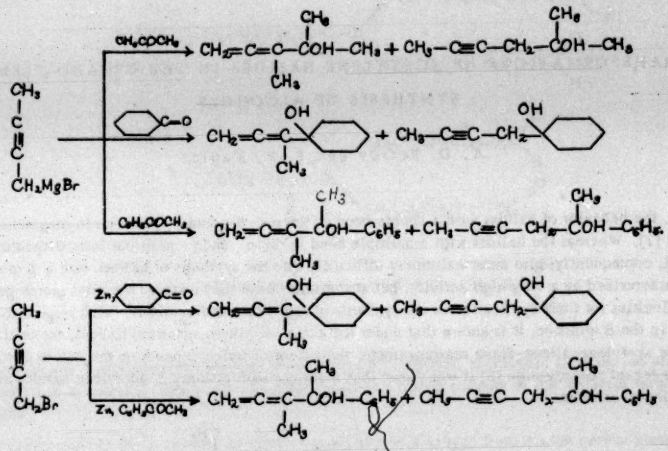
As is known, the behavior of halides with a double bond in the α-, β-, and γ-positions to magnesium has been thoroughly studied [1]. Whereas the halides with a multiple bond in the α- and γ- positions form Grignard reagents with difficulty and, consequently, also enter extremely difficultly into the synthesis of halides with a β-position double bond, they are characterized by a very high activity, but at the same time they undergo the allyl rearrangement, which creates known difficulties for their application in the synthesis of individual hydrocarbons. With respect to the halides with a triple bond in the β-position, it is known that under the action of alkylmagnesium halides, the tertiary acetylene halides undergo the acetylene-allene-diene rearrangement, the extent of which depends on the nature of the Grignard reagent [2]. In our recent investigation [3] it was shown that reactions with primary β-acetylene halides also proceed by an entirely analogous scheme.



By a different method, isomeric transformations were also observed on the action of carbon dioxide on Grignard reagents obtained from the β-acetylene halides. The acid of the allenic structure and a hydrocarbon were formed [4] by the carbonization and hydrolysis of the tertiary acetylene halide.

In a series of works [5-7] it was shown that a mixture of acetylene and allene compounds was formed by the carbonization and hydrolysis of the organomagnesium reagent obtained from primary β-acetylene bromide.

From what has been presented above, it is evident that the β-acetylene halides in their behavior are extremely close to the allyl halides. Their reactions with ketones have still not been studied, but we assumed that they would be entirely analogous to the reaction of the ketones with crotylmagnesium bromide. It is known that with the majority of ketones, only derivatives of the secondary crotyl bromide are obtained, and only in the case of steric hindrance and an incapacity for enolization of hexamethylacetone was a derivative of primary crotyl bromide obtained [8]. Moreover, it seemed strange to us (on consideration of the greater isomerizing activity of zinc halides, compared to the magnesium halides) that Henbest and Jones [9], carrying out the condensation of propargyl bromides with aldehydes and ketones in the presence of zinc, observed no isomerization here and noted the formation of only acetylene alcohols and glycols. Taking into account that these authors were limited in their investigation only to the hydration of the condensation products, which converted the acetylene alcohols to hydroxy ketones (which could not show the presence or absence of allene forms), we studied the condensation of β-acetylene halides with ketones in the presence of both magnesium and zinc in the present investigation. As we also expected, the presence of both acetylene and allene forms in the condensation products was shown on the basis of oxidation and spectral analysis. The reactions investigated can be represented by the equation:



EXPERIMENTAL

1. Reaction of Butyne-2-magnesium Bromide with Cyclohexanone

1-Bromobutyne-2, prepared from butyn-2-ol-1 and PBr_3, had the following constants: b. p. 40-41° at 20 mm, n_D^{20} 1.5093, d_4^{20} 1.5187. 67 g of acetylene bromide was added to 36 g of magnesium and 0.1 g of $HgCl_2$ in 500 ml of ether. Addition of the bromide was continued for 16 hours at 25-30°. Then 48 g of cyclohexanone was added. It was decomposed by ice water and hydrochloric acid. 20 g (26%) of the alcohol was obtained after the usual treatment and 3 distillations.

B. p. 90-92° at 5 mm, n_D^{20} 1.4994, d_4^{20} 0.9696, MR_D 46.06; Calc. for $C_{10}H_{16}O$ 45.90, for $C_{10}H_{16}O$ 46.77. Found %: C 78.09, 78.28; H 10.33, 10.47. $C_{10}H_{16}O$. Calculated %: C 78.95; H 10.52.

In the infrared spectrum were the bands 4.94, 5.8, 4.58 and 6.07 μ, which indicated the presence of allene and acetylene bonds.

Ozonization of the alcohol. Ozonized oxygen was passed for 8 hours through a solution of 6 g of alcohol in 40 ml of dry chloroform. The chloroform solution of the ozonide was poured into 50 ml of water, the mixture was stirred for 2 hours, then 6 ml of 30% hydrogen peroxide was added and the stirring was again continued for 6 hours at 55-60°. The product was neutralized with soda, the chloroform layer was removed, and the aqueous layer was extracted with ether. After drying, the ether and chloroform were driven off. The neutral product was distilled. 2.2 g of a substance with a b. p. of 85-92° was obtained, from which a semicarbazone with a m. p. of 197° was obtained. The melting point of the semicarbazone of methylcyclohexanol-1-ketone was 196° [10]. The aqueous solution of the salts was evaporated, and treated with 10% HCl. The acid was extracted with ether and distilled. Formic acid was found by the calomel method, acetic acid by the cacodyl test. The residue in the flask crystallized. After recrystallization from petroleum ether it melted at 63°. According to the literature, the melting point of cyclohexanol-1-acetic acid was 64° [11].

2. Reaction of Butyne-2-magnesium Bromide with Acetone

67 g of 1-bromobutyne-2 at 20-22° was added during 12 hours to 48 g of magnesium and 0.2 g of $HgCl_2$ in 400 ml of ether. Then 29 g of acetone was added. The reaction proceeded very vigorously. After addition of the acetone stirring was continued for 8 hours more. 18 g (32%) of the alcohol was obtained after the usual treatment.

B. p. 42-44° at 5 mm, n_D^{20} 1.4625, d_4^{20} 0.8745, MR_D 35.22; Calc. for $C_7H_{12}O$ 34.04; for $C_7H_{12}O$ 35.11. Found %: C 74.82, 74.78; H 10.46, 10.55. $C_7H_{12}O$. Calculated %: C 75.00; H 10.71.

Taking of the Raman spectrum showed the presence of frequencies corresponding to double and triple bonds. Taking of the infrared spectrum showed the presence of the bonds: 1920, 1620 and 1570 cm^{-1}.

TABLE 4

Radioactivity of Oxidation Products of 3-C^{14}-Pentane
(Temperature 305°, initial pressure 195 mm; products were removed after 60 seconds).

Products	Weight of sample (mg).	Activity (counts/min.)	Specific activity		
			compounds	for 1 atom	relative (%)
C_5H_{12} (original)	4.3	179 ± 3	96	490	100
	7.9	271 ± 3	102		
	9.2	269 ± 3	96		
	13.2	331 ± 3	104		
CH_2O	6.4	98 ± 3	42	63	13
	7.2	107 ± 3	42		
	11.5	135 ± 5	44		
	29.3	155 ± 2	45		
CH_3CHO	13.9	90 ± 2	29	44	9
	18.4	104 ± 2	31		
	19.9	98 ± 2	30		
	22.6	105 ± 2	31		
CO	11.8	300 ± 6	99	99	20
	12.3	300 ± 6	98		
	16.5	333 ± 10	101		
CO_2	6.3	239 ± 3	100	98	20
	7.2	236 ± 3	95		
	10.5	289 ± 5	98		
	12.9	318 ± 3	102		

TABLE 5

Probabilities of Formation of CH_2O from Different Carbon Atoms of the Hydrocarbon Molecule

Hydrocarbon	Index number of carbon atom					Sum of probabilities
	1	2	3	4	5	
Propane	39	22	39	–	–	100
n-Butane	22	28	28	22	–	100
n-Pentane	17	26.5	13	26.5	17	100

TABLE 6

Probabilities of Formation of CH_3CHO from Different Carbon Atoms of the Hydrocarbon

Hydrocarbon	Carbon atoms				Sum of probabilities
	1-2	2-3	3-4	4-5	
n-Butane	41	18	41	–	100
n-Heptane	43	9	9	43	104

The determined values of the probabilities (in percentages) of the formation of formaldehyde and acetaldehyde are cited in Tables 5 and 6.

As is evident from the data of Table 5, formaldehyde formed not only from the side atoms of the hydrocarbon molecule, but it formed with high probability from all of the carbon atoms of the hydrocarbon chain. For the oxidation of butane and pentane it formed most often from the second carbon atom. This experimental fact was in sharp contradiction to the theory of destructive oxidation.

Exactly the same, it also followed from the data of Table 6 that acetaldehyde may be formed not only from two side atoms of the molecules oxidized, but also from the central atoms.

Thus, in spite of the fact that we sought a reliable basis of the theory of destructive oxidation, our investigations indicated that this theory has no basis.

We propose that the facts observed in the oxidation of hydrocarbons, known at the present time, can be best explained from the point of view of the radical-chain scheme of oxidation developed by N. N. Semenov [7].

According to this scheme, the different hydrocarbon radicals colliding with oxygen molecules can lead to the formation of peroxide radicals, which by their decomposition can form different alcohol radicals and aldehydes. Thus, for example:

3. Reaction of Butyne-2-magnesium Bromide with Acetophenone

67 g of 1-bromobutyne-2 was added to 48 g of magnesium and 0.1 g of $HgCl_2$ in 500 ml of ether. The addition of the bromide was continued for 14 hours at 20-25°. Then 50 g of acetophenone was added during 2 hours, after which the stirring was continued for 3 hours more at 30°. The reaction substance was decomposed and treated as usual. 23 g (27%) of the alcohol was obtained.

B. p. 118-119° at 7 mm, n_D^{20} 1.5450, d_4^{20} 1.0056, MR_D 54.66; Calc. for $C_{12}H_{14}O$ 53.67; for $C_{12}H_{14}O$ 54.60. Found %: C 82.56, 82.68; H 8.48, 8.27. $C_{12}H_{14}O$. Calculated %: C 82.75; H 8.62.

A determination of the infrared spectrum showed the presence of 4.9 and 5.8 μ bands.

4. Reaction of 1-Bromobutyne-2 with Cyclohexanone in the Presence of Zinc

20 g of zinc chips (first treated as indicated in [9], 0.2 g of $HgCl_2$, and 100 ml of anhydrous ether were placed in a flask with a stirrer and reflux condenser, and a mixture of 40 g of 1-bromobutyne-2 and 30 g of cyclohexanone was added dropwise at 30°. A vigorous reaction began after 30 minutes, which then proceeded without heating. On completion of the addition of the mixture the reaction substance was stirred at 30-33° for 3 hours more. It was decomposed with 10% acetic acid. It was treated as usual and distilled. 12 g (45%) of the alcohol, b. p. 110-112° at 20 mm, d_4^{20} 0.9690, n_D^{20} 1.4993 was obtained.

Ozonization. 5.5 g of the alcohol and 40 ml of chloroform were used for the ozonization. Ozonization was continued for 8 hours. Further treatment was carried out just as indicated above. From the neutral products a ketone was isolated, the semicarbazone of which had a m. p. of 197°. The presence of formic acid was determined in the acid portion by the calomel method, and by the cacodyl test the presence of acetic acid was detected. We were unable to detect cyclohexanol-1-acetic acid.

Hydration. A mixture of 2 ml of water, 1 ml of sulfuric acid, 1 g of mercuric sulfate, 15 ml of methyl alcohol and 3 ml of the alcohol obtained was stirred for 8 hours at 60-65°. The methanol was then driven off, and the ketone was extracted with ether. The ether was removed. A semicarbazone with a m. p. of 162° was obtained.

5. Reaction of 1-Bromobutyne-2 with Acetophenone in the Presence of Zinc

A mixture of 20 g of 1-bromobutyne-2 and 24 g of acetophenone was added to 10 g of zinc chips, 0.1 g of $HgCl_2$, and 100 ml of ether at 30°. The reaction was carried out under the same conditions as the preceding synthesis. 5 g of an alcohol with a b. p. of 106-108° at 4 mm, n_D^{20} 1.5455, d_4^{20} 1.0050 was obtained after 3 distillations. A determination of the infrared spectrum showed the presence of frequencies of 1920, 1630 and 1660 cm^{-1}.

Ozonization. 4 g of the alcohol in 30 ml of chloroform was used for the ozonization. Ozonized oxygen was passed for 6 hours. From the neutral products a ketone was isolated, the semicarbazone of which melted at 183°. According to the literature [12] the melting point of the semicarbazone of 2-phenylbutanol-2-one-3 was 183°. Formic and acetic acids were detected in the acid portion of the ozonization product.

The infrared spectra were taken by Yu. P. Egorovy.

SUMMARY

1. The reaction of 1-bromobutyne-2 with acetone, cyclohexanone and acetophenone was carried out in the presence of Mg and Zn.

2. It was shown that in the reactions of β-acetylene bromide with ketones, in the presence of Mg and Zn, the propargyl rearrangement occurred, as a result of which a mixture of acetylene and allene alcohols formed.

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SYNTHESIS OF BRANCHED ALIPHATIC HYDROCARBONS OF $C_{11} - C_{16}$ COMPOSITION VIA THE β-ALKENYL HALIDES

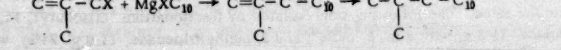
A. D. Petrov and V. M. Melekhin

The positive effect of a multiple bond in the β-position to the halide on the condensation reaction of the alkenyl halides with both alkyl halides and carbonyl compounds, was established in the 70's of the XIX century during the period of the organozinc synthesis of hydrocarbons and alcohols. Thus, M. D. Lvov [1] was unable to obtain n-pentane from n-butyl halide and zinc dimethyl, whereas the synthesis of pentene-1 from allyl iodide and zinc diethyl had already been carried out by A. Würtz. By a similar method, A. M. Zaitsev and coworkers [2] obtained various alkyldiallylcarbinols in high yields by the action of zinc on a mixture of allyl iodide and esters.

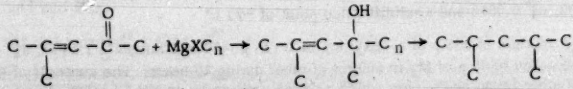
However, wide application of the branched forms of alkenyl halides, with a β-position multiple bond, to the synthesis was attained later – during the period of intensive development of the organomagnesium synthesis in connection with the problem of the investigation and synthesis of high-octane hydrocarbons of the composition $C_6 - C_{12}$, and particularly, in connection with the production of hydrocarbons with quaternary carbon atoms. It was found, for example, that 2,2-dimethylpentane was more preferably obtained via 2,2-dimethylpentene-4, which was synthesized with a yield of 85% (on the basis of allyl bromide) by addition to the latter of an ether solution of tert.-butylmagnesium chloride [3], whereas by the condensation of tert.-butyl chloride with magnesiumpropyl bromide, under both conditions (by heating at about 80° or in the presence of $HgCl_2$), the yield of 2,2-dimethylpentane did not exceed 20%. A. D. Petrov, V. I. Koptev and E. P. Kaplan [4] showed that the steric hindrance of the condensation of a branched ketone with a branched alkyl halide can be overcome by introduction of a multiple bond, instead of in the alkyl halide, into the other component – the ketone – but also in the β-position with respect to the functional group, the carbonyl. Thus, for example, tert.-butylmagnesium chloride, which gave no tertiary alcohol with methyl isobutyl ketone, merely reducing it, reacted with mesityl oxide at 0° with the formation of the corresponding tertiary alcohol.

For the same components, Whitmore [5] showed that while tertiary alkylmagnesium halides add to mesityl oxide at 0° in the 1,2-position, at the boiling point of ether they also add partially in the 1,4-position, which can be used for the purposes of synthesis of hydrocarbons with a double set of consecutive quaternary carbons.

In the present investigation the positive influence of a multiple bond in the β-position to both the halide and also to the carbonyl was first used for the synthesis of a few branched hydrocarbons of $C_{12} - C_{16}$ composition, according to the scheme:



(1)



(2)

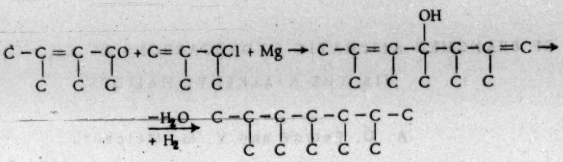
where n = 6 and 10

These hydrocarbons were of interest because, according to known isomerization mechanisms, the isomerization of normal hydrocarbons led chiefly to the formation of 2-methylalkanes and 2,4-dimethylalkanes.

During the synthesis of the above-mentioned hydrocarbons it was found that even the high-molecular, but primary and normal alkyl halides, unlike the tertiary alkyl halides, at the boiling point of ether condensed with mesityl oxide in the 1,4-position only as traces; condensation in the 1,2-position resulted in yields of 32-52%. (Reactions occurred here also with methyl isobutyl ketone, but with yields lower by a factor of 2).

Further, it was found that the simultaneous use in the condensation reaction of both a ketone with a multiple bond in the β-position to the carbonyl and an alkenyl halide with a multiple bond also in the β-position, presented the

possibility of synthesizing 2,3,4,5,6-pentamethylheptane according to Scheme (3). *



(3)

It is interesting and important to note that the condensation of the secondary allyl type halide (3-chloro-2-methylbutene-1) with the above-mentioned unsaturated ketone, unlike the condensation of halides of this type with saturated ketones (for example, diisopropyl ketone [6]), took place without the allyl rearrangement. A similar absence of the allyl rearrangement was also noted in the instance of the condensation of mesityl oxide and methyl isopropenyl ketone with 3-chloro-2-methylbutene-1, which proceeded by a scheme analogous to Scheme (3). For the same condensation of 3-chloro-2-methylbutene-1 with methyl isopropyl ketone, the allyl rearrangement did occur, and led to the formation of two isomeric forms of the tertiary alcohols.

EXPERIMENTAL

2-Methyltridecane. A mixture of 90.5 g of isobutenyl chloride and 110.5 g of decyl bromide (b. p. 77-79° at 2.5 mm, n_D^{20} 1.4551, d_4^{20} 1.0679) dissolved in 400 ml of ether, was added to 50 g of Mg in 300 ml of ether during 3 hours. The mixture was heated at the boiling point of ether for 40 hours, after which it was decomposed with an NH_4Cl solution. By fractionation of the reaction product, 32 g of diisobutenyl (b. p. 113°, n_D^{20} 1.4308), 12 g (41%) of eicosane with a m. p. of 36°, and 40.2 g of 2-methyltridecene-1, b. p. 105-106° at 6 mm, n_D^{20} 1.4395, d_4^{20} 0.7813, were obtained.

Found %: C 85.77; H 14.25. $C_{14}H_{28}$. Calculated %: C 85.63; H 14.37.

Eykman [7], obtaining this olefin by a different reaction (condensation of decylmagnesium halide with acetone), indicated its properties as follows: b. p. 109.5° at 7 mm, n_D^{20} 1.4449, d_4^{20} 0.7845.

The olefin was hydrogenated to 2-methyltridecane over skeletal nickel in methyl alcohol at 103 atm and 115°.

B. p. 108-109° at 7 mm, solidification point −22°, n_D^{20} 1.4273, d_4^{20} 0.7615.
Found %: C 84.75; H 15.24. $C_{14}H_{30}$. Calculated %: C 84.76; H 15.24.

For the purpose of a comparison of the reactivity of isobutenyl chloride and isobutyl chloride, a parallel condensation experiment was carried out with the latter.

A mixture of 46.3 g of isobutyl chloride and 55.3 g of decyl bromide was added to 25 g of Mg in ether. The conditions of the synthesis were the same. The following were isolated by fractionation: diisobutyl, 14.2 g, with a b. p. of 109°, n_D^{20} 1.3925; eicosane, 11.3 g, with a m. p. of 36°; and 2-methyltridecane, 11.9 g (24%), with a b. p. of 108-109° at 7 mm, n_D^{20} 1.4272, d_4^{20} 0.7616 and a solidification point of −21.5°

2,4-Dimethyldecane. A mixture of 378 g of n-hexyl bromide (b. p. 40° at 4 mm, n_D^{20} 1.4477, d_4^{20} 1.1729) and 196.3 g of mesityl oxide were added to 73 g of Mg in 500 ml of ether during 10 hours. The contents of the flask were heated at the boiling point of ether for 30 hours, after which a decomposition by an NH_4Cl solution was carried out. Only traces of the ketone were detected in the reaction products by the action of 2,4-dinitrophenylhydrazine. 10 g of n-dodecane was removed from the reaction products by the action of a solution of urea in methyl alcohol. 169 g of 2,4-dimethyldecen-2-ol-4 (51.2% yield) was then isolated by fractionation.

B. p. 100-101° at 11 mm, n_D^{20} 1.4518, d_4^{20} 0.8473, MR_D 58.64; Calc. 58.67.

A portion of the alcohol was dehydrated by a 45-hour boiling with a mixture of acetic anhydride and sodium acetate, and a portion was dehydrated by distillation over iodine.

* The synthesis was carried out jointly with F. I. Grigoryev.

The 2,4-dimethyldecadiene-2,4, obtained by the first method, had a b. p. of 67-69° at 9 mm, n_D^{20} 1.4497, d_4^{20} 0.7812, but that obtained by dehydration over iodine had a b. p. of 73-76° at 11 mm, n_D^{20} 1.4442, d_4^{20} 0.7816.

The identity of the properties of the resulting diolefin fractions enabled us to reach a conclusion concerning the non-optionality of the dehydration of tertiary olefinic alcohols of this type under the conditions of the Higginbottom method, i. e., by boiling with a mixture of acetic anhydride and sodium acetate. The diolefin was hydrogenated to 2,4-dimethyldecane over skeletal nickel at 128 atm and 130°.

B. p. 74-75° at 11 mm, n_D^{20} 1.4220, d_4^{20} 0.7528, solidification point −84°.
Found %: C 84.65; H 15.47. $C_{12}H_{26}$. Calculated %: C 84.61; H 15.39.

2,4-Dimethylundecane. In the present case, an attempt also to carry out the synthesis by the Yavorsky scheme unlike the preceding case, ended in failure – the original components were recovered. Then from 25 g of Mg and 89.6 g of heptyl bromide a Grignard reagent was obtained, to which 41.2 g of mesityl oxide dissolved in ether (1:1) was also added. The contents of the flask were stirred for 20 hours without heating, after which they were decomposed by ice and by an NH_4Cl solution. After distillation of the ether, 41.4 g of a fraction with a b. p. of 119.4-120.5° at 755 mm, n_D^{20} 1.4140 was obtained. This fraction proved to be an azeotropic mixture of mesityl oxide, heptene-1 and 2-methylpenten-2-ol-4. Obviously, the last two compounds were formed as a result of reduction reactions. By urea, 2.3 g of n-$C_{14}H_{30}$ (m. p. 5°, b. p. 76° at 5 mm, n_D^{20} 1.4293, d_4^{20} 0.7619) was isolated.

38 g (42.6%) of a fraction which proved to be 2,4-dimethylundecen-2-ol-4, was found as a result of a further distillation of the residue.

B. p. 95-96° at 5 mm, n_D^{20} 1.4560, d_4^{20} 0.8530, MR_D 63.21; Calc. 63.30.

10.2 g of 2,4-dimethylundecadiene-2,4, b. p. 75-76° at 5mm, n_D^{20} 1.4480, d_4^{20} 0.7894, was obtained by the dehydration of 20 g of alcohol with 37 g of acetic anhydride and 13 g of sodium acetate.

The diolefin was hydrogenated to 2,4-dimethylundecane in a solution of methyl alcohol over Raney nickel at 150° and 160 atm.

B. p. 72-73° at 8 mm, n_D^{20} 1.4265, d_4^{20} 0.7627, solidification point −68°, MR_D 62.0; Calc. 62.23.
Found %: C 84.58; H 15.46 $C_{13}H_{28}$. Calculated %: C 84.69; H 15.31.

For the purpose of accounting for the role of the multiple bond in the β-position to the carbonyl, 2,4-dimethylundecane was also synthesized via methyl isobutyl ketone. 85.2 g of methyl isobutyl ketone was added to the Grignard reagent obtained from 25 g of Mg and 153 g of n-heptyl bromide, after which the contents of the flask were heated at the boiling point of ether for 20 hours. After decomposition by NH_4Cl and removal of the ether, 65.2 g of a fraction (b. p. 117-119°, n_D^{20} 1.3990, d_4^{20} 0.7171), which proved to be a ternary azeotropic mixture of methyl isobutyl ketone, heptene-1 and methylisobutylcarbinol, was isolated by distillation. The last two compounds were products of reduction reactions. By urea, 4.3 g of n-$C_{14}H_{30}$, with a m. p. of 5°, was isolated. As a result of further distillation, a fraction with a b. p. of 120-122° at 10 mm, n_D^{20} 1.4472, d_4^{20} 0.8421, MR_D 63.59; calc. 63.76, was obtained. This fraction, which corresponded to the tertiary alcohol, was separated in a quantity of 49.8 g (29.3%).

The alcohol was dehydrated according to Higginbottom. 20.2 g of the olefin with a b. p of 101-103° at 10 mm, n_D^{20} 1.4392, d_4^{20} 0.7764, was obtained. The olefin was hydrogenated to 2,4-dimethylundecane in a solution of methyl alcohol at 180° and 220 atm.

B. p. 74-75° at 9 mm, n_D^{20} 1.4258, d_4^{20} 0.7618; solidification point −68.5°.

2,4-Dimethyltetradecane. Here, as also in the preceding instance, no reaction occurred on attempt to carry it out by the Yavorsky scheme. A Grignard reagent was obtained from 25 g of Mg and 82 g of n-$C_{10}H_{21}Br$, and 34.3 g of mesityl oxide dissolved in ether was added to it. After decomposition, and after removal of the ether, 5 g of eicosane was isolated. Then we were able to form about 1.5 g of the 2,4-dinitrophenylhydrazone with a m. p. of 172° (apparently formed from the saturated ketone 4,4-dimethyltetradecanone-2, obtained as a result of addition in the 1,4-position); the melting point of the 2,4-dinitrophenylhydrazone of mesityl oxide was 201-203°. The tertiary alcohol here was quantitatively dehydrated during the synthesis, and 25.2 g (32.3%) of the corresponding diolefin, 2,4-dimethyltetradecadiene-2,4, was separated by distillation.

B. p. 108-109° at 3 mm, n_D^{20} 1.4606, d_4^{20} 0.8114.

The diolefin was hydrogenated to 2,4-dimethyltetradecane in methyl alcohol over Raney nickel at 130° and 210 atm.

B. p. 119-120° at 4 mm, n_D^{20} 1.4340, d_4^{20} 0.7757, solidification point −37.5°.
Found %: C 84.86; H 15.45. $C_{16}H_{34}$. Calculated %: C 84.86; H 15.14.

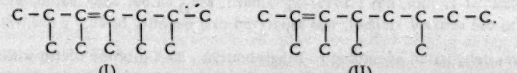
2,3,4,5,6-Pentamethylheptane. 72 g of 2,3-dimethylpenten-2-one-4 (b. p. 146-147°, n_D^{20} 1.4472, d_4^{20} 0.8678) was obtained according to Kondakov [8] from 108 g of acetyl chloride and 98 g of trimethylethylene. Then, with stirring, a mixture of 94 g of 3-chloro-2-methylbutene-1 and 72 g of 2,3-dimethylpenten-2-one-4, dissolved in 300 ml of ether, was added to 50 g of Mg in 300 ml of ether, according to the Yavorsky scheme. The reaction products were stirred without heating for 70 hours, after which they were decomposed with an NH_4Cl solution and ice. After removal of the ether, under atmospheric pressure, and the decadiene fraction of about 65° at 7 mm, 56 g (48%) of a fraction was obtained (b. p. 76-77° at 7 mm, n_D^{20} 0.4710, d_4^{20} 0.8833, MR_D 57.69; calc. 58.21), which corresponded to the reaction product, the tertiary alcohol, 2,3,4,5,6,-pentamethylheptadien-1,5-ol-4 (or for the isomerization of the allyl halide—2,3,4,6-tetramethyloctadien-2,6-ol-4).

15 g of the alcohol was oxidized with a 2% solution of $KMnO_4$. Acetone (2,4-dinitrophenylhydrazone with a m. p. of 125°, a test of a mixture with the 2,4-dinitrophenylhydrazone of known acetone gave no depression) and diacetyl (a 2,4-dinitrophenylhydrazone with a m. p. of 314-315°), were identified in the neutral oxidation products. In the concentrated solution of the salts only formic acid (acetic acid was not detected) was found, which was determined quantitatively by the calomel method; it was found to be 1.1613 g. Since acetone, diacetyl and acetic acid would also be obtained by the oxidation of 2,3,4,6-tetramethyloctadien-2,6-ol-4, we could determine the absence of this isomer only by the data of the investigation of the acid fraction. Fortunately, during further study we were able to obtain additional demonstrations of the absence of this alcohol and, consequently, of the allyl rearrangement also, in the condensation of the allyl halide with an unsaturated ketone.

40 g of 2,3,4,5,6-pentamethylheptadien-1,5-ol-4 was boiled for 30 hours, with 69 g of acetic anhydride and 27 g of sodium acetate. 15.3 g of a fraction (b. p. 55-56° at 7 mm, n_D^{20} 1.4650, d_4^{20} 0.8118, MR_D 55.95; calc. 56.22), which corresponded to the triolefin 2,3,4,5,6-pentamethylheptatriene-1,3,5, and 10.2 g of the unaltered alcohol, were obtained. 15 g of the resulting dodecatriene was hydrogenated over Raney nickel in a methyl alcohol solution at 160° and 120 atm. The hydrogenation product had the following properties: b. p. 60-68° at 10 mm, n_D^{20} 1.4418, d_4^{20} 0.7862. It readily decolorized bromine water. The presence of one double bond in the hydrogenation product was also confirmed by the Raman spectra and by the results of an elementary analysis.

Found %: C 85.25; H 14.69. $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37. $C_{12}H_{26}$. Calculated %: C 84.61; H 15.39.

Taking into account that tetra-substituted ethylenes are hydrogenated much more difficultly than are the di-substituted ethylenes [9], and also that the difficulty of hydrogenation increases with the shifting of the multiple bond to the center of the molecule [10], we assumed that the resulting hydrogenate had the structure, 2,3,4,5,6-pentamethylheptene-3 (I), with an admixture of 2,3,4,6-tetramethyloctene-2 (II), if even a partial allyl rearrangement of the allyl halide occurred on condensation of the unsaturated ketone with an allyl halide.



(I) (II)

For the purpose of establishment of the structure of the olefin, it was oxidized with $KMnO_4$. Oxidation proceeded with difficulty, and the hydrocarbon was not oxidized in the cold even by a 6% solution of $KMnO_4$. The hydrocarbon was oxidized by boiling at 100° for 10 days. From 4.7 g of the hydrocarbon, the following neutral oxidation products were obtained (no acid oxidation products were detected): 1st fraction, 77-98°, 0.2 g, n_D^{20} 1.3881; 2nd fraction, 120-130°, 0.2 g, n_D^{20} 1.4134; 3rd fraction, 62-65° at 10 mm, 1.4 g, n_D^{20} 1.4412. For the 2,4-dinitrophenylhydrazone, the 1st fraction gave a precipitate with a m. p. of 116-117° (after 4 recrystallizations); a test of a mixture with the 2,4-dinitrophenylhydrazone of known methyl isopropyl ketone gave no depression. The 2nd fraction yielded a 2,4-dinitrophenylhydrazone with a m. p. of 101-102°. As is known from the literature [11], the 2,4-dinitrophenylhydrazone of 2,3-dimethylpentanone-4 had this melting point. The absence of acetone and the ketone of C_9 composition in the oxidation products was a demonstration of the absence of 2,3,4,6-tetramethyloctene-2 in the olefin studied and, consequently, was also an additional demonstration that no allyl rearrangement occurred on condensation of the allyl halide with the unsaturated ketone. The 3rd fraction proved to be the non-oxidized olefin. Over a more active catalyst than nickel—palladium on silica gel—at 124 atm and 163° we were able to convert it to the paraffin hydrocarbon, 2,3,4,5,6-pentamethylheptane.

B. p. 64-66° at 11 mm, n_D^{20} 1.4392, d_4^{20} 0.7838, Solidification point < −80°.
Found %: C 84.82; H 15.47. $C_{11}H_{26}$. Calculated %: C 84.61; H 15.39.

2,3,4,6-Tetramethylheptane. The reaction was carried out under the conditions indicated above. 36.5 of Mg, and a mixture of 36.6 g of 3-chloro-2-methylbutene-1 with 29.4 g of mesityl oxide, were used. After removal of the ether, 28.0 g (55.5%) of a fraction which corresponded to 2,3,4,6-tetramethylheptadien-1,5-ol-4 was isolated (or 2,4,6-trimethyloctadien-2,6-ol-4 in the event of the allyl rearrangement of the initial halide to the primary).

B. p. 87-88° (19 mm), n_D^{20} 1.4560, d_4^{20} 0.8695, MR_D 53.50; calc. 53.59.

7 g of the alcohol was oxidized by a 2% solution of $KMnO_4$. The following fractions of neutral oxidation products were obtained: 1st, b. p. 48-60°, 0.3 g, n_D^{20} 1.3602; 2nd, b. p. 81.5-92°, 0.5 g, n_D^{20} 1.3942; 3rd, b. p. 85-89° at 19 mm, 2.2 g, n_D^{20} 1.4639. The 1st fraction gave a 2,4-dinitrophenylhydrazone, with a m. p. of 125° (from alcohol). A test of a mixture gave no depression with the 2,4-dinitrophenylhydrazone of acetone. The 2nd fraction gave the mono-2,4-dinitrophenylhydrazone of diacetyl, with a m. p. of 199° (from ethyl acetate).
Found %: N 21.42. $C_{10}H_{10}O_8N_4$. Calculated %: N 21.05.

0.9182 g of formic acid was determined by the calomel method. The concentrated, aqueous solution of the salts of the acids was decomposed with 2% H_2SO_4, and the acids were extracted with ether. On removal of the ether, 0.7 g of a fraction with a b. p. of 62-68° at 10 mm, n_D^{20} 1.4288, was obtained. The 2,4-dinitrophenylhydrazone obtained from it had a m. p. of 216° (the 2,4-dinitrophenylhydrazone of pyruvic acid had a m. p. of 218°).

The presence of diacetyl and the absence of acetic acid in the oxidation products indicated the absence of 2,4,6-trimethyloctadien-2,6-ol-4 in the alcohols studied, and served as a new instance of confirmation that the condensation of an allyl halide with an unsaturated ketone was not accompanied by an allyl rearrangement.

20.5 g of 2,3,4,6-tetramethylheptadien-1,5-ol-4 was dehydrated, according to Higginbottom, for 14 hours. 14.2 g of a fraction with a b. p. of 66° at 21 mm (n_D^{20} 1.4660, d_4^{20} 0.8033, MR_D 51.80; calc. 51.60) was obtained, which corresponded to 2,3,4,6-tetramethylheptatriene-1,3,5, which was hydrogenated to 2,3,4,6-tetramethylheptane over palladium at 110° and 125 atm.

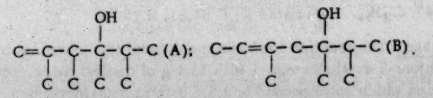
B. p. 173-174°, n_D^{20} 1.4260, d_4^{20} 0.7581, MR_D 52.83; calc. 53.00.

2,3,4,5-Tetramethylhexane. A mixture of 23.0 g of 3-chloro-2-methylbutene-1 and 16.8 g of methyl isopropenyl ketone (b. p. 96-96.5°, n_D^{20} 1.4208) was added during 1 hour to 25 g of Mg covered with ether, according to Yavorsky. The contents of the flask were stirred for 12 hours, after which they were decomposed with NH_4Cl and ice. On removal of the ether, 14.0 g (45.5%) of a fraction with a b. p. of 73-74° at 19 mm, n_D^{20} 1.4615, d_4^{20} 0.8792, which corresponded to 2,3,4,5-tetramethylhexadien-1,5-ol-3 was isolated. On dehydration of the latter over iodine, 9.4 g of 2,3,4,5-tetramethylhexatriene-1,3,5, b. p. 154-155°, n_D^{20} 1.4580, d_4^{20} 0.8108, was obtained. By hydrogenation of this triolefin over palladium at 160° and 170 atm, 2,3,4,5-tetramethylhexane (b. p. 156°, n_D^{20} 1.4208, d_4^{20} 0.7503) was obtained, which had been synthesized earlier by a different scheme [12].

For the purpose of a comparison of the course of the reaction in the instance of the saturated ketone, a condensation of 3-chloro-2-methylbutene-1 with methyl isopropyl ketone was carried out. 68.8 g of methyl isopropyl ketone (b. p. 94-95°, n_D^{20} 1.3868, d_4^{20} 0.8039) in 150 ml of ether was added to the Grignard reagent from 75 g of Mg and 104.6 g of 3-chloro-2-methylbutene-1 in 1 liter of ether. The following main fractions were obtained: 1st, b. p. 185-188°, 43.0 g (34.7%), n_D^{20} 1.4585, d_4^{20} 0.8568; and 2nd, b. p. 188-192°, 4.2 g (8.3%), n_D^{20} 1.4597, d_4^{20} 0.8589.

10 g of a fraction with a b. p. of 185-188° was oxidized by a 1% solution of $KMnO_4$. The neutral products were extracted with ether, and carefully dried with Na_2SO_4. On removal of the ether, the following fractions were obtained: 1st, b. p. 78-88°, 0.8 g, n_D^{20} 1.3892; 2nd, b. p. 90-98°, 1.4 g, n_D^{20} 1.3873. The 2,4-dinitrophenylhydrazone of diacetyl, with a m. p. of 314-315°, was obtained from the 1st fraction. The 2nd fraction yielded a 2,4-dinitrophenylhydrazone with a m. p. of 116°. A test mixture of it with the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone melted at 115.5°. 0.5910 g of formic acid was determined by the calomel method. A solution of the salts of the acids was evaporated to dryness, decomposed by 20% H_2SO_4, and the acids were extracted with ether. On removal of the ether, the residue (0.1 g) had the odor of acetic acid. An amide with a m. p. of 81° was obtained. The melting point of the amide of acetic acid was 82°.

The presence of diacetyl and formic acid in the oxidation products corresponded to alcohol (A), and the presence of a small quantity of acetic acid indicated a possible admixture of the (B) form.



4 g of a fraction with a b. p. of 188-192° was oxidized by a 1% solution of $KMnO_4$. The following fractions were obtained from the neutral oxidation products: 1st, b. p. 82-89°, 0.3 g; 2nd, b. p. 89-96°, 0.8 g, n_D^{20} 1.3854. Both fractions gave a 2,4-dinitrophenylhydrazone with a m. p. of 116°, which corresponded to the 2,4-dinitrophenylhydrazone of methyl isopropyl ketone. The acidic oxidation products gave the fractions: 1st, b. p. 102-121°, 0.3 g; and 2nd, b. p. 72-82° at 24 mm, 0.2 g. The amide of the 1st fraction had a m. p. of 81.5°. The 2,4-dinitrophenylhydrazone of the 2nd fraction had a m. p. of 214.5°. According to the resulting oxidation products, the fraction consisted of (B) alcohols.

SUMMARY

1. For the first time, 2-methyltridecane, 2,4-dimethyldecane, 2,4-dimethylundecane, 2,4-dimethyltetradecane, 2,3,4,6-tetramethylheptane and 2,3,4,5,6-pentamethylheptane were synthesized, and the physical properties of these hydrocarbons were studied.

2. For the organomagnesium synthesis it was found that the use of the little known branched hydrocarbon-halides or ketones with a double bond in the β-position to the functional group gave 2 times higher yields, compared to the synthesis via the saturated halides or ketones.

3. It was shown that a halide of the allyl type (3-chloro-2-methylbutene-1), undergoing the allyl rearrangement on condensation with a saturated ketone (methyl isopropyl ketone), did not undergo this rearrangement on condensation with unsaturated ketones with a multiple bond in the β-position to the carbonyl (methyl isopropenyl ketone, mesityl oxide, etc.), which presents the possibility of synthesizing hydrocarbons with 4,5 and a larger number of consecutive methyl groups by the method indicated.

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TERTIARY TRIATOMIC ALCOHOLS OF THE ACETYLENE SERIES AND THEIR TRANSFORMATIONS

VII. HYDROGENATION OF 2,3,6-TRIMETHYLHEPTYNE-4-TRIOL-2,3,6; 3,4,7-TRIMETHYLOCTYNE-5-TRIOL-3,4,7; 2-METHYL-5-(1-HYDROXCYCLOHEXYL)-HEXYNE-3-DIOL-2,5 AND 2,4-DI-(1-HYDROXYCYCLOHEXYL)-BUTYNE-3-OL-2

V. I. Nikitin and I. M. Timofeeva

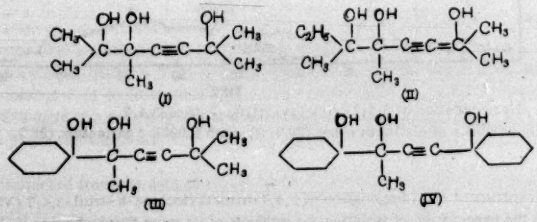
Having at our disposal a convenient method of production of the acetylene series glycerols [1,2], we decided to synthesize tertiary ethylenic glycerols, not described in the chemical literature, by the catalytic hydrogenation of acetylenic glycerols. For this purpose, it was of interest, first of all, to test platinum and palladium catalysts. It was necessary to find out whether, in the presence of these catalysts, or one of them, the hydrogenation of the acetylenic glycerols proceeded selectively to such a degree that upon stopping the introduction of hydrogen after the passage of one mole of hydrogen per mole of the alcohol, a pure ethylenic glycerol could be obtained.

From the voluminous literature available on the hydrogenation of different unsaturated compounds, it is known that alcohols of acetylene [3-5], vinylacetylene [6-8], diacetylene [3], and also acetylene glycols and their esters [9-15], in the presence of a platinum catalyst, are readily hydrogenated to the corresponding saturated compounds. No instances when it would be impossible to bring the hydrogenation of oxygen-containing acetylene derivatives to complete saturation in the presence of a platinum catalyst are available in the literature. Only two instances are known for the unsaturated hydrocarbons, namely, diphenyldiacetylene, the hydrogenation of which stopped with the formation of the diethylene compound [16], and tetraphenylethylene, which could not be hydrogenated further [17].

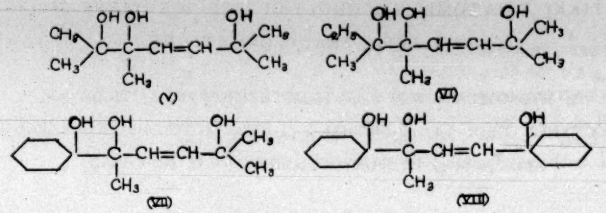
With respect to the palladium catalyst, in the majority of cases in its presence the hydrogenation of these compounds also proceeds to complete saturation, but with palladium the hydrogenation acts more selectively than it does with platinum; not allowing, or almost not allowing the hydrogenation of an ethylenic compound while acetylenic molecules are present, it can sometimes be used as a catalyst in the synthesis of ethylenic derivatives from acetylenic compounds. However, palladium also does not always favor the production of ethylenic alcohols from acetylenic alcohols, since often, although to a lesser degree than platinum, it can bring about the hydrogenation of ethylenic alcohols simultaneously with acetylenic alcohols.

In the presence of a palladium catalyst, only the tertiary vinylacetylene alcohols with complex radicals [7] showed inabilities to hydrogenate beyond the formation of the ethylenic alcohols.

In the present work the hydrogenation of the following four representatives of the tertiary triatomic alcohols of the acetylene series was carried out: 2,3,6-trimethylheptyne-4-triol-2,3,6 (I), 3,4,7-trimethyloctyne-5-triol-3,4,7 (II), 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (III) and 2,4-di-(1-hydroxycyclohexyl)-butyne-3-ol-2 (IV).



The hydrogenation was carried out over platinum oxide (according to Adams) and over palladium on chalk. It was found that all four of the acetylenic alcohols hydrogenated with an appreciable rate only to the ethylenic triatomic alcohols (V, VI, VII, VIII), not only over palladium, but also over platinum catalysts.



When the hydrogenation was not interrupted on addition of 50% of the hydrogen, it ceased somewhat later, adding still a certain additional quantity of hydrogen. For the hydrogenation of the glycerol with two cyclohexyl radicals (IV), for example, this excess hydrogen amounted to 17%. In a methanol solution we were unable to continue the reaction if no additional catalyst was added. However, when the hydrogenation was carried out in an acetic acid medium, it could be continued further, if after each cessation of the reaction we introduced a new portion of catalyst; moreover, the absorption of hydrogen could be brought to 100% and more, but no saturated glycerols were obtained. We arrived at the same results by hydrogenating a purified ethylenic glycerol in an acetic acid medium over a platinum catalyst.

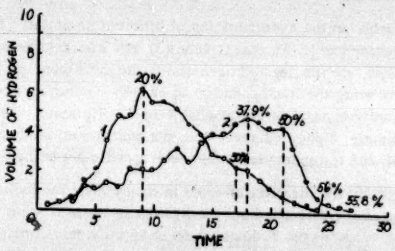


Fig. 1. Hydrogenation of 2,3,6-trimethylheptyne-4-triol-2,3,6 at 30°.
1) With 0.0006 g of platinum oxide; 2) with 0.0008 g of palladium.

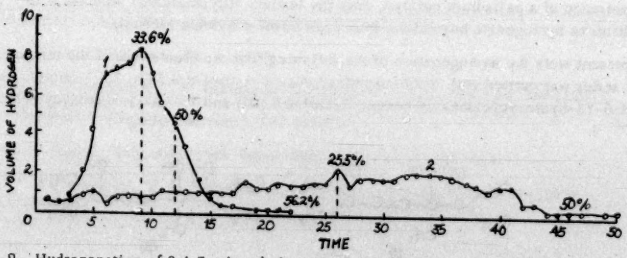


Fig. 2. Hydrogenation of 3,4,7-trimethyloctyne-5-triol-3,4,7.
1) With 0.0006 g of platinum oxide (30°); 2) with 0.0008 g palladium (28°).

We carried out an experiment of hydrogenation of 3,4,7-trimethyloctene-5-triol-3,4,7 (VI) over P_2O in an acetic acid medium with the expectation of isolating the products of its more thoroughgoing hydrogenation. However,

we were unable to isolate any homogeneous product. A somewhat widely-boiling fraction was obtained, the elementary composition of which, like the number of hydroxyl groups determined by the Chugaev-Tserevitinov method, convinced us that the hydrogenation of 3,4,7-trimethyloctene-5-triol-3,4,7 resulted due to the replacement of its hydroxyl groups by hydrogen.

A picture of the hydrogenation rate of the acetylenic glycerols which we studied is offered by suitable curves • (Figs. 1,2,3 and 4). Curve 1 was taken over a platinum catalyst, and Curve 2 was taken over palladium. These curves were constructed by S. V. Lebedev's method, i. e., the time, in minutes, was plotted on the abscissa, and the quantity of hydrogen, in milliliters, consumed during each minute, was plotted on the ordinate.

In all cases, for the hydrogenation we used the same quantity of the substance, 0.002 mole of the alcohol, and the following quantities of catalyst: platinum oxide, by calculation of 3 g per 1 mole of the alcohol, and palladium precipitated on chalk, by calculation of 4 g of prepared catalyst per 1 mole of the alcohol. The experiments were carried out at a pressure of 688.4 mm. Hydrogenation was carried out in the usual "duck" attached to a shaker. Methanol (10 ml), first distilled over caustic alkali, was used as the solvent. The reading of hydrogen was made from a burette for 100 ml (H_2 54.9 ml, $2H_2$ 109.8 ml).

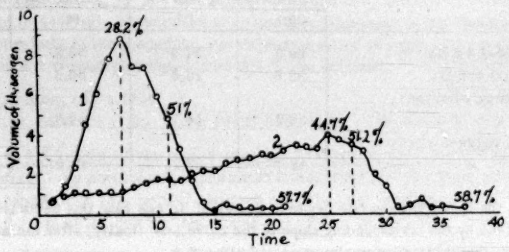


Fig. 3. Hydrogenation of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5. 1) With 0.003 g of platinum oxide (30°); 2) with 0.008 g of palladium (28°).

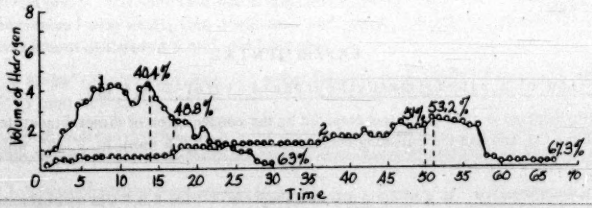


Fig. 4. Hydrogenation of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2. 1) With 0.003 g of platinum oxide (30°); 2) with 0.008 g of palladium (28°).

From a consideration of these curves it follows that the hydrogenation rate of the acetylene series tertiary triatomic alcohols is greater over a platinum catalyst than over a palladium catalyst. In the series of alcohols considered, the 3,4,7-trimethylocytne-5-triol-3,4,7 (II) (Fig. 2) hydrogenated over platinum oxide most rapidly of all. In hydrogenation rate, 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (III) (Fig. 3) followed after it. Then came 2,3,6-trimethylheptyne-4-triol-2,3,6 (I) (Fig. 1), and the hydrogenation of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 (IV) (Fig. 4) took place slowest of all.

• The curves were constructed from the data of one of many experiments carried out for each acetylenic triol.

Over palladium, 2,3,6-trimethylheptyne-4-triol-2,3,6 (I) hydrogenated most rapidly of all, after which was the alcohol with one cyclohexyl radical (III), then 3,4,7-trimethyloctyne-5-triol-3,4,7 (II), and in hydrogenation rate, the acetylenic glycerol with two cyclohexyl substituents (IV) stood last. We see that the order for this hydrogenation remains almost the same, as for that over platinum, except that 3,4,7-trimethyloctyne-5-triol-3,4,7 and 2,3,6-trimethylheptyne-4-triol-2,3,6 exchanged places.

In all instances the curves reflected the general character of the hydrogenation inherent to the acetylene series tertiary triatomic alcohols, which we hydrogenated, independently of which of the two catalysts was used for the hydrogenation. This general character resulted from the fact that, with both catalysts, hydrogenation proceeded with an appreciable rate only as far as the formation of ethylenic glycerols. The hydrogenation started with an increasing rate. Over the platinum catalyst it went much more rapidly than over palladium. With an increasing rate, for the platinum catalyst from 20% hydrogen for the heptynetriol to 40% for the triol with two cyclohexyl radicals, added; for the palladium catalyst, from 25% for the octynetriol to 53% for the bicyclic, added, as is evident from the tables.

Maximum Quantity of Hydrogen Adding with an Increasing Rate and During the Total Time of Hydrogenation

Name of alcohol hydrogenated	Hydrogen added (in %)			
	With increasing rate		during total time of hydrogenation	
	Pt	Pd	Pt	Pd.
2,3,6-Trimethylheptyne-4-triol-2,3,6 (I)	20.0	37.9	56.0	55.8
3,4,7-Trimethyloctyne-5-triol-3,4,7 (II)	33.6	25.5	56.0	50.0
2-Methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (III)	28.2	44.7	57.7	58.7
2,4-Di-(1-hydroxycyclohexyl)-butyn-3-ol-2 (IV)	40.4	53.2	63.0	67.3

Reaching its maximum, the hydrogenation rate began to decrease. In one case this decrease was more rapid, in another slower, than was observed by the corresponding slope of the curve, and finally, after the addition of somewhat more than 50% of the hydrogen, the hydrogenation almost ceased altogether.

The formation of cis-trans isomers should be expected in the hydrogenation of the acetylene series glycerols to ethylenic glycerols. However, in each of the hydrogenations which we carried out, only one isomer was isolated, to which the cis-form should be attributed. The cis-structure follows from the fact that all of the ethylene series glycerols obtained, as we established [18], are quite readily cyclized to the substituted dihydropyranols with the formation of one molecule of water.

EXPERIMENTAL

1. Hydrogenation of 2,3,6-Trimethylheptyne-4-triol-2 3,6 (I)

2,3,6-Trimethylheptyne-4-triol-2,3,6 was prepared by the condensation of dimethylacetylenecarbinol with dimethylacetylcarbinol [1], and had the following constants: b. p. 122° (2.5 mm), m. p. 82°, which corresponds to the literature value.

a) Over a platinum catalyst. 10 g of 2,3,6-trimethylheptyne-4-triol-2,3,6 was hydrogenated over 0.16 g of platinum oxide in 60 ml of methanol at 16° and 690.9 mm. The calculated quantity of hydrogen for hydrogenation to the double bond amounted to 1408 ml. 1420 ml was absorbed during 14 minutes, after which the reaction stopped. The catalyst was filtered off, the alcohol was removed from the reaction products, and the product which remained crystallized on standing. Recrystallized several times from benzene, it melted at 116-117°. 9 g (90%) of the pure product was obtained.

b) Over a palladium catalyst. 10 g of 2,3,6-trimethylheptyne-4-triol-2,3,6 was hydrogenated over 0.16 g of palladium on chalk in 60 ml of methanol at 18° and 698 mm. The calculated quantity of hydrogen for hydrogenation to the double bond amounted to 1408 ml. 1450 ml was absorbed during 25 minutes, after which the reaction stopped. The catalyst was filtered off, the alcohol was removed from the reaction products; crystallizing on standing, the hydrogenation products were recrystallized several times from benzene. Their m. p. was 116-117°, and the yield was 9.4 g (94%).

The products formed by the hydrogenation of 2,3,6-trimethylheptyne-4-triol-2,3,6 over a platinum and a palladium catalyst, were identical, as was established by the melting point of a sample of a mixture, and corresponded to cis-2,3,6-trimethylheptene-4-triol-2,3,6, which was not described in the literature.

Found %: C 63.82, 63.63; H 10.97, 10.70; OH 25.5. $C_{10}H_{20}O_3$. Calculated %: C 63.83; H 10.64; OH 27.0.

2. Hydrogenation of 3,4,7-Trimethyloctyne-5-triol-3,4,7 (II)

3,4,7-Trimethyloctyne-5-triol-3,4,7 was prepared by the condensation of methylethylacetylcarbinol with dimethylacetylenecarbinol [2]

B. p. 118-119° (2 mm), n_D^{20} 1.4794, which corresponds to the literature value.

a) Over a platinum catalyst. 30.7 g of 3,4,7-trimethyloctyne-5-triol-3,4,7 was hydrogenated over 0.1 g of platinum oxide in 60 ml of methanol at 30° and 682.5 mm. The calculated quantity of hydrogen for hydrogenation to the double bond amounted to 4250 ml, and was passed during 185 minutes, after which hydrogenation ceased. The catalyst was filtered off and the solvent was removed. The product was dissolved in ether and dried with sodium sulfate. The ether was removed and the product was vacuum distilled. 28 g (92%) of a substance was distilled, which consisted of the ethylene series glycerol, cis-3,4,7-trimethyloctene-5-triol-3,4,7, which was not described in the literature.

B. p. 117-118° (2 mm), d_4^{20} 1.0051, n_D^{20} 1.4774, MR_D 56.83. $C_{11}H_{22}O_3$. Calculated 57.11.

b) Over a palladium catalyst. 40 g of 3,4,7-trimethyloctyne-5-triol, dissolved in 60 ml of methanol, was hydrogenated over 0.1 g of palladium at 30° and 685.0 mm. The calculated quantity of hydrogen for hydrogenation to a double bond amounted to 4970 ml. Hydrogenation ceased after absorption of the theoretical quantity of hydrogen, and the product, treated similarly to the preceding, was vacuum distilled at 2 mm. 37.3 g (92%) of a substance, which also proved to be cis-3,4,7-trimethyloctene-5-triol-3,4,7, was obtained.

B. p. 117-118° (2 mm), n_D^{20} 1.4774.
Found %: C 65.19, 64.90; H 11.29, 10.99; OH 26.9. $C_{11}H_{22}O_3$. Calculated %: C 65.35; H 10.90; OH 25.2.

Hydrogenation of 3,4,7-Trimethyloctene-5-triol-3,4,7 (VI) (b. p. 117-118° at 2 mm) over a platinum catalyst in an acetic acid medium. By preliminary experiments it was found that in a methanol solution 3,4,7-trimethyloctene-5-triol (VI) hydrogenated over neither platinum nor palladium catalysts; therefore, the hydrogenation was carried out in an acetic acid solution, and platinum oxide was used as the catalyst.

10 g of the trimethyloctenetriol was hydrogenated in the presence of 0.05 g of platinum oxide in 30 ml of acetic acid at 28° and 691.6 mm. The calculated quantity of hydrogen required for saturation amounted to 1440 ml. 200 ml was absorbed during 30 minutes, after which the reaction was stopped. The reaction resumed on addition of a new portion of catalyst. Thus, 0.32 g of platinum oxide was introduced in four portions. In all, 1600 ml of hydrogen was absorbed, after which the reaction stopped. The catalyst was filtered off, and the acid was distilled from the reaction products under a water-jet pump. The substance which remained was dissolved in ether. The ether solution was washed with a soda solution and with water, then it was dried over potash, and after removal of the ether the hydrogenation products were vacuum distilled at 3 mm into fractions:

1st fraction, b. p. 83-84° (3 mm) n_D^{20} 1.4604, 2.5 g; 2nd fraction, b. p. 84-86° (3 mm), n_D^{20} 1.4565, 1.5 g; 3rd fraction, b. p. 86-115° (3 mm), n_D^{20} 1.4772, 2.5 g.

8.9 g of 3,4,7-trimethyloctene-5-triol-3,4,7 in the second experiment and 10 g in the third experiment, were hydrogenated exactly the same. The similar fractions of each experiment were combined and vacuum distilled.

As a result, the following fractions were obtained:

1st fraction, b. p. 80-83° (3 mm), n_D^{20} 1.4605; 2nd fraction, b. p. 83-84° (3 mm), n_D^{20} 1.4618; 3d fraction, b. p. 84-86° (3 mm), n_D^{20} 1.4624; 4th fraction b. p. 86-90° (3 mm), n_D^{20} 1.4600; 5th fraction, b. p. 90-94° (3 mm), n_D^{20} 1.4578; 6th fraction, b. p. 96-97° (3 mm), n_D^{20} 1.4560.

In all the fractions, with the exception of the first, the number of hydroxyl groups was determined according to Chugaev-Tserevitinov. In all cases it proved to be somewhat lower than resulted for the octanetriol, which showed that the hydrogenation was accompanied by reduction of the hydroxyl group.

2nd fraction, b. p. 83-84° (3 mm); 0.1119 g substance: 35.3 ml CH_4 (29.5°, 685.2 mm). Found %: OH 19.52.
3rd fraction, b. p. 84-86° (3 mm); 0.1005 g substance: 33.9 ml CH_4 (28.5°, 684.3 mm). Found %: OH 21.8.
4th fraction, b. p. 86-90° (3 mm); 0.0782 g substance: 25.5 ml CH_4 (29.7°, 685.2 mm). Found %: OH 20.16.
5th fraction, b. p. 90-94° (3 mm); 0.1042 g substance: 36.2 ml CH_4 (30.5°, 683.7 mm). Found %: OH 21.38.
6th fraction, b. p. 96-97° (3 mm); 0.0902 g substance: 29.1 ml CH_4 (29.5°, 685.2 mm). Found %: OH 19.96, $C_{11}H_{24}O_3$. Calculated %: OH 18.0. $C_{11}H_{24}O_3$. Calculated %: OH 25.5.

An elementary analysis was carried out for the 3rd and 5th fractions, the results of which confirmed the deduction that the hydrogenation of an ethylenic glycerol is accompanied by a replacement of the hydroxyl group by hydrogen.

3rd fraction 0.0934 g substance: 0.2424 g CO_2; 0.1073 g H_2O. 0.1305 g substance: 0.3398 g CO_2; 0.1463 g H_2O. Found %: C 70.77, 70.81; H 12.74, 12.40.

5th fraction 0.0997 g substance: 0.2610 g CO_2; 0.1163 g H_2O. Found %: C 71.41; H 12.93. $C_{11}H_{24}O_2$. Calculated %: C 64.20; H 11.76. $C_{11}H_{24}O_3$. Calculated %: C 70.21; H 12.76.

In the hydrogenation experiments just described, somewhat more than 2 moles of hydrogen per 1 mole of the substance hydrogenated was passed. In order to eliminate any doubt concerning whether reduction hydrogenation began after the calculated quantity of hydrogen for complete saturation of the unsaturated compound was absorbed, we carried out a hydrogenation with the theoretical quantity of hydrogen.

8.3 g of 3,4,7-trimethyloctene-5-triol-3,4,7 was hydrogenated over 0.1 g of platinum oxide in 50 ml of acetic acid at 20° and 694.2 mm. 475 ml of hydrogen was absorbed after 45 minutes and the reaction was stopped, after which a new portion of catalyst was added. In all, after each cessation of the reaction, 0.215 g of catalyst was introduced. The calculated quantity of hydrogen required for saturation was 1080 ml. 1080 ml of hydrogen was absorbed. The subsequent treatment was carried out according to the preceding one. The product was distilled at 3.5 mm into the following fractions:

1st fraction, b. p. 100-103°, n_D^{20} 1.4602, 0.6 g; 2nd fraction, b. p. 103-105°, n_D^{20} 1.4609, 1.2 g; 3rd fraction, b. p. 105-110°, n_D^{20} 1.4600, 1.0 g; 4th fraction, b. p. 114-116°, n_D^{20} 1.4590, 0.5 g; 5th fraction, b. p. 116-118°, n_D^{20} 1.4594, 1.0 g 6th fraction, b. p. 148-149°, n_D^{20} 1.4635, 0.4 g; 7th fraction, b. p. 149-150°, n_D^{20} 1.4750, 2.2 g.

The number of hydroxyl groups was determined in the 3rd fraction.

0.1078 g substance: 34.2 ml CH_4 (21°, 693.7 mm). Found %: OH 20.4. $C_{11}H_{24}O_3$. Calculated %: OH 25.5. $C_{11}H_{24}O_2$. Calculated %: OH 18.0.

Thus, in this instance, a still more widely boiling mixture was obtained, and many fractions were similar to those obtained in the first instance of the hydrogenation of 3,4,7-trimethyloctene-5-triol-3,4,7. Hence, it could be concluded that the ethylenic tertiary triatomic alcohol 3,4,7-trimethyloctene-5-triol-3,4,7 in an acetic acide medium over platinum oxide had the capacity for only the so-called reduction hydrogenation due to the replacement of its hydroxyl groups by hydrogen.

3. Hydrogenation of 2-Methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 (III)

2-Methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 was prepared by the condensation of dimethylacetylenecarbinol with acetycyclohexanol.

B. p. 151-155° (3 mm), m. p. 87-88°, which correspond to the literature values [2].

a) Over a platinum catalyst. 10 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 was hydrogenated in the presence of 0.13 g of platinum oxide in 60 ml of methanol at 19° and 693.4 mm. The calculated quantity of hydrogen for hydrogenation to a double bond amounted to 1161 ml. 1175 ml was absorbed, during 17 minutes, after which the reaction ceased. The catalyst was filtered off, the alcohol was removed from the reaction products, and the product which remained crystallized on standing. Recrystallized several times from benzene, it melted at 102-103°, and amounted to 9.8 g (98%).

b) Over a palladium catalyst. 10 g of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 was hydrogenated in the presence of 0.13 g of palladium on chalk in 60 ml of methanol at 22° and 690.6 mm. The calculated quantity of hydrogen to a double bond was 1179 ml. 1175 ml was absorbed during 40 minutes, after which the reaction slowed considerably and stopped. The catalyst was filtered off, the alcohol was removed from the reaction products, and the product which remained crystallized on standing. After several recrystallizations from benzene, 9.9 g (99%) of a substance with a m. p. of 102-103° was obtained.

The products formed by the hydrogenation of 2-methyl-5-(1-hydroxycyclohexyl)-hexyne-3-diol-2,5 over platinum and palladium catalysts were identical (established by test of a mixture) and corresponded to cis-2-methyl-5-(1-hydroxycyclohexyl)-hexene-3-diol-2,5, which was not described in the literature.

Found %: C 68.78, 68.61; H 10.65, 10.87; OH 22.67, 22.29. $C_{13}H_{24}O_3$. Calculated %: C 68.42; H 10.53; OH 22.56.

4. Hydrogenation of 2,4-Di-(1-hydroxycyclohexyl)-Butyn-3-ol-2 (IV)

2,4-Di-(1-hydroxycyclohexyl)-butyn-3-ol-2 was prepared by the condensation of acetylcyclohexanol with acetylenecyclohexanol. Its m. p. was 107-108°, which corresponded to the literature value [2].

a) Over a platinum catalyst. 10 g of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 was hydrogenated in the presence of 0.11 g of platinum oxide in 60 ml of methanol at 18° and 695.6 mm. The calculated quantity of hydrogen for hydrogenation to a double bond amounted to 1147 ml. 1090 ml was absorbed during 22 minutes, after which the reaction slowed considerably and stopped. The catalyst was filtered off, the alcohol was removed from the reaction products, and the product which remained crystallized on standing. Recrystallized from benzene, it melted at 111-112°. 10 g (100%) was obtained.

b) Over a palladium catalyst. 10 g of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 was hydrogenated in the presence of 0.11 g of palladium on chalk in 60 ml of methanol at 17° and 695.6 mm. The calculated quantity of hydrogen for hydrogenation to a double bond amounted to 1140 ml. 1150 ml was absorbed during 120 minutes, after which the reaction slowed down sharply and stopped. The catalyst was filtered off, the alcohol was removed from the reaction products, and the product which remained crystallized on standing. After several recrystallizations from benzene, 10 g (100%) of a substance with a m. p. of 111-112° was obtained.

The products formed by the hydrogenation of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 over a platinum and a palladium catalyst were identical, as was established by a test of a mixture, and proved to be cis-2,4-di-(1-hydroxycyclohexyl)-buten-3-ol-2 which was not described in the literature.

Found %: C 71.98, 72.02; H 10.34, 10.43; OH 18.04, 18.67. $C_{16}H_{28}O_3$. Calculated %: C 71.64; H 10.44; OH 19.17.

SUMMARY

1. Tertiary glycerols of the acetylene series were hydrogenated in the presence of platinum or palladium catalysts to glycerols of the ethylene series which, in a steric respect, formed only one, obviously, the cis-form.

2. The hydrogenation rate curves of the acetylene series tertiary glycerols obtained over both of the catalysts had the same character. However, for the platinum catalyst the hydrogenation rate was somewhat greater, compared with that of the hydrogenation over palladium.

3. The ethylene series tertiary glycerols were unable to hydrogenate to the corresponding saturated glycerols either over platinum oxide or over palladium precipitated on chalk.

4. Absorption of hydrogen by the ethylene series glycerols took place in an acetic acid solution in the presence of platinum oxide; however, it proceeded due to the replacement of the hydroxyl groups of these glycerols by hydrogen.

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INVESTIGATION IN THE FIELD OF ALKANESULFONIC ACIDS

XIV. SYNTHESIS AND PROPERTIES OF ACETYL AND BENZOYL AMIDES OF 2-METHYLPROPANE- AND 2-METHYLBUTANESULFONIC ACIDS

A. G. Kostsova

The synthesis of the acetyl and benzoyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids is described in the present paper. As already recorded in previous papers [1], the benzoyl amides of the lower alkanesulfonic acids have a sweet taste, but this characteristic disappears with an increase of the radical chain. Thus, it was shown that the benzoyl amides of methane-, ethane-, chloromethane- and α-chloroethanesulfonic acids are intensely sweet compounds, and the benzoyl amide of 2-methylethanesulfonic acid is moderately sweet, whereas the benzoyl amide of butanesulfonic acid is completely tasteless. The benzoyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids, which we obtained and described in the present papers, like the benzoyl amide of butanesulfonic acid, were tasteless.

As also described earlier, the acetyl amides, synthesized together with the benzoyl amides, had a sour taste, which was retained independently of the size and nature of the acid radical.

Unlike the neutral aryl amides, the acetyl and benzoyl amides described were clearly expressed acids with a pH of 3.3-3.9, were able to form completely stable metallic salts, and were soluble in water without appreciable hydrolysis, both at room temperature and on heating.

EXPERIMENTAL*

The initial sulfochlorides were obtained by the usual method [1].

Production of the amides of 2-methylpropane- and 2-methylbutanesulfonic acids. Dry, gaseous ammonia was passed into a solution of 5.5 g of 2-methylpropane sulfochloride in 35 ml of anhydrous ether, with cooling to -5 -7°, until cessation of the formation of an ammonium chloride precipitate. On completion of the reaction the precipitate was filtered off, and the ether was driven off on the water bath. After removal of the ether the amide remained in the flask as a viscous, brown liquid, which did not distill without decomposition.

According to the literature, 2-methylpropane sulfamide melted at 14-16° [2]. The amide which we obtained did not crystallize. The yield of the crude amide was 3.25 g. It was readily soluble in water, alcohol and benzene, and was insoluble in ligroin. A 3.3 g yield of 2-methylbutane sulfamide was obtained from 6 g of the sulfochloride by the same method.

Production of the acetyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids. 3.25 g of 2-methylpropane sulfamide and 2.4 ml of acetyl chloride (30 % excess) were refluxed on the water bath with two condensers connected in series. A viscous, brown substance, which solidified in the cold, was formed. The product was recrystallized from carbon tetrachloride. Its yield was 1.92 g (41%).

The acetamide of 2-methylpropanesulfonic acid was a colorless, crystalline substance of sour taste. Its m. p. was 67-68°, its pH was 3.2, it was soluble in the cold in water, alcohol, benzene, acetone and ether and it dissolved on heating in carbon tetrachloride.

0.0488 g substance: 2.6 ml 0.1 N H_2SO_4. 0.1020 g substance: 0.1302 g $BaSO_4$. Found %: N 7.51; S 17.50. $C_6H_{13}O_3NS$. Calculated %: N 7.80; S 17.80.

The acetamide of 2-methylbutanesulfonic acid was synthesized by an analogous method. From 3.3 g of the amide and 3.1 ml of acetyl chloride 1.24 g (32.6%) of the pure acetamide was obtained. Its m. p. was 55-57°, it was soluble in the same solvents, and its pH was 3.7.

* G. S. Agapova participated in the experimental part.

0.0797 g substance: 3.9 ml 0.1 N H_2SO_4. 0.0528 g substance: 0.0634 g $BaSO_4$. Found %: N 6.99; S 16.49. $C_7H_{15}O_3NS$. Calculated %: N 7.25, S 16.58.

Production of the benzoyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids. 1.8 g of 2-methylpropane sulfamide and 1.5 ml of benzoyl chloride (30% excess) were refluxed on an oil bath at 135-150° for 2 hours. The viscous, brown substance which formed was transferred to a crystallizer. Crystallization was observed after evaporation of the excess benzoyl chloride. The solid product was treated with dilute alkali. The insoluble resinous portion was filtered off, and the benzoyl amide of 2-methylpropanesulfonic acid was precipitated from the alkaline solution by dilute sulfuric acid. Its yield was 1.57 g (75.8%). It was recrystallized from alcohol and water. The crystals were colorless. Their m. p. was 74-76°, they were highly soluble in alcohol, ether, benzene, acetone, and carbon tetrachloride, and difficultly soluble in water; their pH was 3.32; they were tasteless.

0.0502 g substance; 1.99 ml 0.1 N H_2SO_4. 0.1018 g substance: 0.0971 g $BaSO_4$. Found %: N 5.50; S 13.09. $C_{11}H_{15}O_3NS$. Calculated %: N 5.80; S 13.27.

The benzoyl amide of 2-methylbutanesulfonic acid was obtained by the same method. The yield of the pure product from 2.4 g of the amide and 2.7 ml of benzoyl chloride was 3.32 g (78.6%). It consisted of colorless, tasteless crystals. Its m. p. was 71-72° and its pH was 3.0.

0.0712 g substance; 2.7 ml 0.1 N H_2SO_4. 0.1342 g substance: 0.1202 g $BaSO_4$. Found %: N 5.42; S 12.30. $C_{12}H_{17}O_3NS$. Calculated %: N 5.52; S 12.50.

Production of the sodium salts of the acyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids. The sodium salts of the acetyl and benzoyl amides were obtained by the same method. The properties of the salts were similar. 0.5 g of the acetamide of 2-methylpropanesulfonic acid was dissolved in anhydrous ether. 0.064 g of metallic sodium was added in small portions to the solution. The formation of a white precipitate was observed. After all of the sodium had reacted the precipitate was filtered off and dried. The yield was 0.4 g (72.4%). The sodium salt of 2-methylpropanesulfonic acid was an amorphous, white powder; it did not melt above 200°, and it dissolved in water, but did not hydrolyze.

0.0402 g substance: 1.9 ml 0.1 N H_2SO_4. Found %: N 6.76. $C_6H_{12}O_3NSNa$. Calculated %: N 6.96.

0.43 g (78.3%) of the sodium salt of the acetamide of 2-methylbutanesulfonic acid was obtained from 0.5 g of the acetamide and 0.059 g of metallic sodium.

0.0382 g substance: 1.6 ml 0.1 N H_2SO_4. Found %: N 6.05. $C_7H_{14}O_3NSNa$. Calculated %: N 6.51.

0.4 g (70.7%) of the sodium salt of the benzoyl amide of 2-methylpropanesulfonic acid was obtained from 0.5 g of the amide and 0.047 g of metallic sodium.

0.0308 g substance: 1.08 ml 0.1 N H_2SO_4. Found %: N 4.92. $C_{11}H_{14}O_3NSNa$. Calculated %: N 5.32.

0.394 g (72.5%) of the sodium salt of the benzoyl amide of 2-methylbutanesulfonic acid was obtained from 0.5 g of the benzoyl amide and 0.045 g of metallic sodium.

0.0200 g substance: 0.78 ml 0.1 N H_2SO_4. Found %: N 5.51. $C_{12}H_{16}O_3NS$. Calculated %: N 5.54.

SUMMARY

1. The acetyl and benzoyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids were obtained and characterized for the first time.

2. For the first time, the sodium salts of the acetyl and benzoyl amides of 2-methylpropane- and 2-methylbutanesulfonic acids were obtained and their properties were studied.

3. It was shown that the resulting benzoyl amides were tasteless. This confirmed the hypothesis that, with an increase of the radical chain, the sweet taste of these compounds diminished and finally disappeared.

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PREPARATIVE METHOD OF THE SYNTHESIS OF CYANOHYDRINS

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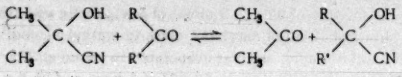
As is known, the usual methods of synthesis of the cyanohydrins are based on the reaction of carbonyl compounds with anhydrous hydrocyanic acid or alkali metal cyanides.

In the literature there is one patent specification [1] on the feasibility of the production of cyanohydrins by the reaction of aldehydes and ketones with other cyanohydrins, which emerge in the role of hydrogen cyanide carriers. Acetone cyanohydrin has been used recently for the synthesis of cyanohydrins of some steroid ketones [2,3], and also as a source of hydrogen cyanide in different addition reactions [4-6]. However, the reaction of cyanohydrins with the simplest carbonyl compounds have been little studied, and apart from the above-mentioned patent there are no literature data on this problem.

We studied the reaction of different aldehydes, ketones and acetoacetic ester with acetone cyanohydrin in the presence of alkali catalysts and organic bases, both at room temperature and on heating (60-70°).



This reaction is reversible and leads to the establishment of an equilibrium, which depends on the dissociation constants of the initial and final cyanohydrins, and also on the possibility of the removal of one of the components from the reaction zone. The method described gives better results the lower the dissociation constant and the solubility of the resulting cyanohydrin. The autocatalytic reaction of acetone cyanohydrin with the 4-piperidones, which leads to the formation of a theoretical yield of the cyanohydrins of the 4-piperidones at room temperature, proceeds most readily. This reaction is also facilitated by the low solubility of the resulting cyanohydrins of the 4-piperidones, which precipitate from the reaction mixture as colorless crystals. Acetone cyanohydrin also reacts very readily with the cyclohexanones, forming an 85-90% yield of the cyanohydrins of the latter. Somewhat poorer results were obtained in the reaction of acetone cyanohydrin with aldehydes (formic, propionic, butyric, benzoic), aliphatic ketones (methyl ethyl ketone, butyrone, isobutyrone), cyclopentanones, tetrahydro-4-pyrones and acetoacetic ester; moreover, the corresponding cyanhydrins formed with a yield of 60-80%, but it was sometimes expedient to carry out the reaction with removal of the acetone which formed (shift of equilibrium toward the cyanohydrin which formed). We were unable to obtain the cyanohydrins of aliphatic-aromatic and aromatic ketones of the acetophenone type and of α-tetralone by this method, since their dissociation constants exceeded by many times the dissociation constant of acetone cyanohydrin. With the exception of the instances indicated, it is possible readily to obtain various cyanohydrins by means of acetone cyanohydrin, and in a preparative respect this method has many advantages over the old methods.

EXPERIMENTAL

The acetone cyanohydrin used in the syntheses had the following constants: b. p. 65-67° (7 mm), n_D^{19} 1.400.

A saturated solution of potash in methyl alcohol at 20°, which contained about 3-4% of potash, was most often used as the catalyst. Aqueous solutions of potash, and also triethylamine or piperidine, were used in some experiments.

Methyl ethyl ketone cyanohydrin. A mixture of 14.4 g (0.2 mole) of methyl ethyl ketone (b. p. 78-79°), 17 g (0.2 mole) of acetone cyanohydrin, and 5 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and on the next day was acidified with concentrated sulfuric acid until it was slightly acid to Congo. After removal of the acetone and methyl alcohol at 55-60°, 7 ml of catalyst was again added (alkaline reaction), and the mixture was left overnight at 20°. We repeated this operation twice. Then the solution was neutralized with concentrated sulfuric acid and was vacuum distilled. Moreover, 13.3 g of methyl ethyl ketone cyanohydrin with an admixture of acetone

cyanohydrin (b. p. 84-89° at 19 mm, n_D^{22} 1.4105) was obtained. We were unable to separate the pure methyl ethyl ketone cyanohydrin by distillation.

Butyrone cyanohydrin. A mixture of 22.8 g (0.2 mole) of butyrone (b. p. 141.5-143°), 51 g (0.6 mole) of acetone cyanohydrin and 25 ml of catalyst (potash in methyl alcohol) was left overnight at 20°; then it was acidified with concentrated sulfuric acid, and the acetone and methyl alcohol were vacuum distilled at 20 mm (without heating). Another 25 ml of catalyst was added to the residue, and after standing for a night at 20° the mixture was acidified with concentrated sulfuric acid, the acetone and methyl alcohol were evaporated in vacuo and the reaction substance was distilled.

37.5 g of acetone cyanohydrin (b. p. 80-86° at 22 mm) was recovered, and 15.8 g of buytrone cyanohydrin was isolated:

B. p. 84-84.5° (3 mm), n_D^{20} 1.4335, d_4^{20} 0.9040, MR 40.61; calc. 40.48.

Literature values [7]: B. p. 119° (21 mm), n_D^{18} 1.4336, d^{18} 0.9077.

Isobutyrone cyanohydrin. A mixture of 22.8 g (0.2 mole) of isobutyrone (b. p. 124-125°), 51 g (0.6 mole) of acetone cyanohydrin and 20 ml of catalyst (potash in methyl alcohol) was heated for 5 hours at 65-70°, after which it was left overnight at 20°. After acidification with concentrated sulfuric acid, the acetone and methyl alcohol were vacuum distilled at 20°, and then 40 g of the initial acetone cyanohydrin with a b. p. of 56-58° at 5 mm was distilled. On cooling, the residue crystallized. The resulting crystals were dissolved in ether, washed with water, and the ether was evaporated in vacuo. 20 g of isobutyrone cyanohydrin was obtained, which, after recrystallization from ether, melted at 59-59.5°. The literature value of the m. p. was 59° [8].

Acetoacetic ester cyanohydrin. A mixture of 39 g (0.3 mole) of acetoacetic ester (b. p. 78-80° at 20 mm), 76.5 g (0.9 mole) of acetone cyanohydrin and 45 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, then it was acidified with concentrated sulfuric acid, and was evaporated in vacuo at 20°. As a result of the vacuum distillation, 65 g of acetone cyanohydrin was recovered (b. p. 56-58° at 5 mm) and 30.6 g of acetoacetic ester cyanohydrin was isolated:

B. p. 87.5-88° (2.5 mm), n_D^{20} 1.4338, d_4^{20} 1.0823, MR 37.78; calc. 37.52.

Literature values [7]: B. p. 127-128° (16.5 mm), $n_D^{13.5}$ 1.4355, $d^{13.5}$ 1.0886.

Butyraldehyde cyanohydrin. A mixture of 18 g (0.25 mole) of butyraldehyde (b. p. 72-75°), 63.75 g (0.75 mole) of acetone cyanohydrin and 20 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and on the next day was vacuum distilled (after acidification). 44 g of acetone cyanohydrin (b. p. 53-60° at 4 mm) was obtained, and 20.4 g of butyraldehyde cyanohydrin was isolated.

B. p. 73-74° (3 mm), n_D^{20} 1.4220, d_4^{20} 0.9397, MR 26.72; calc. 26.63.

Literature values [9]: B. p. 110.5-111° (20.5 mm), $n_D^{15.5}$ 1.4226, $d^{15.5}$ 0.9434.

Propionaldehyde cyanohydrin. A mixture of 29 g (0.5 mole) of propionaldehyde (b. p. 47.5-50°), 85 g (1 mole) of acetone cyanohydrin and 50 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and then after acidification it was vacuum distilled. 50 g of acetone cyanohydrin (b. p. 52-58° at 3 mm) was recovered, and 29 g of propionaldehyde cyanohydrin was obtained:

B. p. 62-64° (3 mm), n_D^{20} 1.4150, d_4^{20} 0.9610, MR 22.16; calc. 22.01.

Literature values [9]: B. p. 102-103° (23 mm), n_D^{18} 1.4174, d_4^{15} 0.9690.

Formaldehyde cyanohydrin. a) 43 g of a 35-37% aqueous solution of formaldehyde, 42.5 g (0.5 mole) of acetone cyanohydrin and a solution of 0.5 g of potash in 5 ml of water, mixed, with cooling by snow, was left overnight in thawing snow, then was acidified with concentrated sulfuric acid, and was evaporated to one-third its volume on a steam bath, and then in vacuo at 20°. The residue was extracted 6 times with ether, the ether extract was carefully dried with anhydrous $CuSO_4$, and the ether was removed. 20 g of formaldehyde cyanohydrin was obtained by vacuum distillation; its b. p. was 77-79° (3.5 mm), $n_D^{22.5}$ 1.4108.

b) 13.2 g (0.44 mole) of paraform was dissolved in 34 g (0.4 mole) of acetone cyanohydrin by heating at about 40-42°, and 10 ml of catalyst was added (potash in methyl alcohol). The mixture was left at 20° for 1.5 hours, then it was acidified with concentrated sulfuric acid and was evaporated, at first on a steam bath, and later in vacuo at 20°. Extraction of the residue by ether, drying by anhydrous $CuSO_4$ and vacuum distillation yielded 18.1 g of formaldehyde cyanohydrin:

B. p. 76.5-78° (3 mm), n_D^{20} 1.4112.

Literature values [9]: B. p. 103° (16 mm), n_D^{19} 1.4118.

On mixture of 28.5 g (0.5 mole) of formaldehyde cyanohydrin and 150 ml (1.5 moles) of concentrated hydrochloric acid, a vigorous boiling began, and then the mixture was crystallized and was left overnight at 20°. On the next day we heated the reaction substance for 2 hours on a boiling water bath, and after cooling, it was extracted with ether in a percolator for 15 hours. After removal of the ether and after two recrystallizations from ether, 9.5 g of glycolic acid with a m. p. of 78.3-79° was obtained.

Literature values: m. p. 78° [10], m.p. 80° [11].

Benzaldehyde cyanohydrin. A mixture of 31.8 g (0.3 mole) of benzaldehyde (b. p. of 178-179°), 25.5 g (0.3 mole) of acetone cyanohydrin and 10 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and on the next day it was acidified with concentrated sulfuric acid, and the acetone and methyl alcohol were vacuum distilled. The residue was diluted with an equal volume of ether, washed 2 times with water, 2 times with a saturated solution of bicarbonate, and the original benzaldehyde was removed by shaking with a saturated solution of sodium bisulfite. After drying the ether solution by sodium sulfate, removal of the ether and drying the residue (3 hours) in a vacuum of 10 mm at 70°, 35.8 g of benzaldehyde cyanohydrin was obtained as an oil, which solidified in a cooling mixture (ice + salt), and which we were unable to recrystallize.

Literature values: m. p. 21.5-22° [9], m. p. 20° [12].

On mixture of 4 g of benzaldehyde cyanohydrin with 5 ml (0.05 mole) of concentrated hydrochloric acid, the mixture simmered and then was crystallized and left overnight at 20°. On the next day the mixture was diluted with 4 ml of water, heated for 2 hours on a boiling water bath, and on cooling was extracted six times with ether. From the ether extract, after its drying by sodium sulfate, 2.8 g of mandelic acid was isolated, which after recrystallization from benzene melted at 116-118°.

Literature values [13]: m. p. 118°.

Cyclohexanone cyanohydrin. A mixture of 78.4 g (0.8 mole) of cyclohexanone (b. p. 157°), 136 g (1.6 mole) of acetone cyanohydrin and 20 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and then after acidification was vacuum distilled. 53.3 g of acetone cyanohydrin (b. p. 87-95° at 25 mm) was recovered, and 85.9 g of cyclohexanone cyanohydrin was isolated, which after recrystallization from petroleum ether melted at 34-36°.

B. p. 86-91° (3 mm), n_D^{25} 1.4638.

Literature values: B. p. 129-130° (16 mm), m. p. 27° [14], m. p. 29° [7].

By the hydrolysis of 50 g (0.4 mole) of cyclohexanone cyanohydrin, by means of 60 ml (0.6 mole) of concentrated hydrochloric acid, followed by a 6-hour extraction with ether in a percolator, 56.8 g of 1-cyclohexanol carboxylic acid was obtained, which after recrystallization from petroleum ether melted at 108-109°.

Literature values: m. p. 107° [15], m. p. 108-109° [16].

Similar results were also obtained by the use of triethylamine and piperidine as the catalyst (0.01 mole per 1 mole of acetone cyanohydrin).

1-Methylcyclohexanone cyanohydrin. A mixture of 22.4 g (0.2 mole) of 1-methylcyclohexanone (b. p 166°), 34 g (0.4 mole) of acetone cyanohydrin and 20 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and on the next day was vacuum distilled (after acidification). 16.3 g of acetone cyanohydrin (b. p. 55-63° at 4 mm) was recovered, and 25.1 g of 1-methylcyclohexanone cyanohydrin was obtained, possibly as a mixture of the stereoisomers:

B. p. 92.5-93.5° (3 mm), n_D^{19} 1.467.

On cooling by a cooling mixture, 11 g of the crystalline isomer was isolated, which after two recrystallizations from n-heptane melted at 53.5-54°.

Found %: N 10.27, 10.12. $C_8H_{13}ON$. Calculated %: N 10.22.

A fraction with a b. p. of 99-100.5° (4 mm), $n_D^{19.5}$ 1.4671, was separated by vacuum distillation of the noncrystallizing residue.

Found %: N 10.77, 10.82. $C_8H_{13}ON$. Calculated %: N 10.22.

On long freezing, a small quantity of the crystalline isomer was separated from the liquid fraction.

Literature values [14]: b. p. of mixture 126-130° (15 mm), n_D^{16} 1.467; crystalline isomer m. p. 53-54°; liquid isomer b. p. 126° (15 mm), n_D^{16} 1.467.

1-Methylcyclopentanone cyanohydrin. A mixture of 4.9 g (0.05 mole) of 1-methylcyclopentanone (b. p. 139°), 21.25 g (0.25 mole) of acetone cyanohydrin and 10 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and then after acidification was vacuum distilled. 16.6 g of acetone cyanohydrin (b. p. 49-52° at 3 mm) was recovered, and 4.4 g of 1-methylcyclopentanone cyanohydrin was separated:

B. p. 85-86° (2.5 mm), n_D^{11} 1.4602.

Literature values [14]: B. p. 122-124° (19 mm), n_D^{12} 1.461.

2,2-Dimethyltetrahydro-4-pyrone cyanohydrin. A mixture of 12.8 g (0.1 mole) of 2,2-dimethyltetrahydro-4-pyrone [17] (b. p. 178-179°), 25.4 g (0.3 mole) of acetone cyanohydrin and 10 ml of catalyst (potash in methyl alcohol) was left overnight at 20° and on the next day it was acidified and vacuum distilled. At the same time, 14.5 g of acetone cyanohydrin (b. p. 55.5-58° at 4 mm) was recovered, and from the residue on washing with NaCl solution 10.1 g of 2,2-dimethyltetrahydro-4-pyrone cyanohydrin precipitated, which after recrystallization from ether had a m. p. of 88-89° and gave no melting point lowering with a sample obtained in our laboratory by the usual method.

1,2,5-Trimethyl-4-piperidone cyanohydrin. From a mixture of 14.1 g (0.1 mole) of 1,2,5-trimethyl-4-piperidone [18] (b. p. 55° at 4 mm), 10.2 g (0.12 mole) of acetone cyanohydrin and 10 ml of water, on standing overnight at 20° and subsequent dilution with water, 16.6 g of 1,2,5-trimethyl-4-piperidone cyanohydrin precipitated, which after recrystallization from ethyl acetate had a m. p. of 127-129° and gave no melting point depression with a known sample obtained in our laboratory by the usual method.

1,3-Dimethyl-4-piperidone cyanohydrin. From a mixture of 12.7 g (0.1 mole) of 1,3-dimethyl-4-piperidone [8] (b. p. 73-75° at 17 mm) and 10.2 g (0.12 mole) of acetone cyanohydrin, after standing overnight at 20°, 15.3 g of 1,3-dimethyl-4-piperidone cyanohydrin precipitated, which after recrystallization from ethyl acetate and after drying in vacuo melted at 84.5-86°.

Found %: N 17.71, 17.76. $C_8H_{14}ON_2$. Calculated %: N 18.11.

α-Trans-decalone cyanohydrin. A mixture of 6 g (0.04 mole) of α-trans-decalone (m. p. 33°), 17 g (0.2 mole) of acetone cyanohydrin and 10 ml of catalyst (potash in methyl alcohol) was left overnight at 20°, and then was acidified with concentrated sulfuric acid. Acetone and methyl alcohol were evaporated in vacuo, and 10.6 g of acetone cyanohydrin (b. p. 48-50° at 3 mm) was recovered. The residue was diluted with a twofold quantity of ether, washed carefully with water and dried with Na_2SO_4. After removal of the ether an oil which crystallized was obtained, from which after separation and recrystallization from n-heptane, 3.6 g of α-trans-decalone cyanohydrin with a m. p. of 80.5-81.5° was isolated.

Literature values [19]: m. p. 82°.

SUMMARY

1. A preparative method of cyanohydrin synthesis was developed by means of an exchange reaction between the acetone cyanohydrin and ketones and aldehydes of the aliphatic, aromatic, carbocyclic and heterocyclic series.

2. A dependence of the yields on the dissociation constants and solubilities of the cyanohydrins was shown.

3. Cyanohydrins of methyl ethyl ketone, butyrone, isobutyrone, formaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, cyclohexanone, 1-methylcyclohexanone, 1-methylcyclopentanone, 2,2-dimethyltetrahydro-4-pyrone, 1,2,5-trimethyl-4-piperidone, 1,3-dimethyl-4-piperidone and α-trans-decalone were obtained by the method developed.

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MOBILITY OF SULFUR IN 2-MERCAPTO DERIVATIVES OF BENZIMIDAZOLE, BENZOXAZOLE AND BENZOTHIAZOLE

L. V. Sulima, A. F. Rekasheva and G. P. Miklukhin

In the present study the influence of the molecular structure of organic sulfur-containing compounds on the mobility of the sulfur atoms contained in them was studied by the method of isotope exchange on the basis of the 2-mercapto derivatives of benzimidazole, benzoxazole and benzothiazole. In addition to theoretical significance, such a study is of interest with respect to the problem of the mechanism for accelerating the rubber vulcanization process, since it is known that 2-mercaptobenzothiazole (Captax) is widely used as a vulcanization accelerator, the analogous oxazole derivative is not a typical accelerator, while the 2-mercaptobenzimidazole is already used as an antioxidant.

The exchange of sulfur between the above indicated compounds and elementary sulfur was studied under homogeneous conditions.

EXPERIMENTAL

The individual charges of 0.002 mole of Captax and 0.002 mole of radioactive sulfur were placed into ampoules, each containing 6 ml of toluene, and the mixtures heated at 150°. The 2-mercaptobenzoxazole and 2-mercaptobenzimidazole were subjected to exchange reaction at 130 and 150° in toluene-alcohol solutions (2 ml of alcohol and 4 ml of toluene). The exchange substances and solvents had previously been carefully purified; the starting mercapto derivatives had melting points corresponding to those given in the literature [7] (179, 195 and 298°, respectively). The radioactive sulfur was recrystallized from carbon disulfide and benzene.

The separation of the components after exchange was achieved by repeated extraction of the toluene solutions with aqueous 0.5% sodium hydroxide solution (in the case of the oxazole and thiazole derivatives) and with 1% ammonia solution (in the exchange experiments with 2-mercaptobenzimidazole). The exchanged compounds were precipitated from the alkaline solutions by acidification with hydrochloric acid. The reprecipitation was repeated no less than three times. After thorough washing with water and drying, the separated compounds had the same melting points as the starting compounds. After extracting the mercapto derivatives from them the toluene solutions were evaporated at room temperature, and the liberated sulfur was first repeatedly washed with methyl alcohol, after which it was recrystallized from ethyl alcohol and, finally, from benzene.

Before determining the activity of the starting sulfur, the sulfur after exchange, and the sulfur entering into the composition of the organic compounds, were converted into sodium sulfate by the Carius oxidation method. The experimental results are given in Tables 1 and 2 and in Figs. 1 and 2. In these Tables are given the average number of impulses, recorded by the meter in 1 minute with 4 mg amounts of benzidine sulfate, distributed uniformly over exactly the same area on the paper supports.

The equilibrium activity (x_{∞}) was calculated by the usual radioactive isotope balance equation from the found activity of the starting sulfur and the molecular ratio of sulfur to Captax. The degree of exchange z (in percent of the equilibrium exchange) was calculated by two methods – by the activity of the Captax sulfur and by the reduction in the activity of the elementary sulfur. The averages of these values are given in the Tables. The difference between them failed to exceed 5-6%.

The divergence in the radioactive isotope balance, characterizing the over-all accuracy of the measurements at all of the experimental stages, is 3-6%, and in only one case did it reach 9% (Experiment 5, Table 2).

The exchange velocity constants were found with the aid of the usual equation for the kinetics of isotope exchange. From Figs. 1 and 2 it can be seen that the values of $-\ln\left(1-\frac{x}{x_{\infty}}\right)$ as a function of time are satisfactorily plotted on straight lines, passing through the coordinate origin. The energy of activation for the studied exchange reactions was calculated by the Arrhenius equation. The values of the exchange velocity constants and of the energies of activation are given in Table 3.

TABLE 1

Exchange Reaction with Elementary Sulfur at 150°

Experiment No.	Duration of Heating (Hrs.)	Activity: In original sulfur (Found)	Activity: At Full Exchange (Calculated)	Activity: In the Organic Compound (Found)	Activity: In the Sulfur After Exchange (Found)	Percent Exchange	k (hr.$^{-1}$)	Difference in Radioactive Isotope Balance (%)
2-Mercaptobenzothiazole								
a) Concentration of sulfur and 2-mercaptobenzothiazole 0.33 mole/liters; solvent toluene								
1	1	2860	1430	290	2400	36	0.446	−5
2	2	2860	1430	348	2050	52	0.366	−4
3	5	2860	1430	570	1710	80	0.321	+3
4	8	2860	1430	673	1550	93	0.332	+1
					Average		0.365	
b) Concentration of sulfur and 2-mercaptobenzothiazole 0.11 mole/liter; solvent toluene								
5	2	2820	1410	182	2280	31	0.185	−6
6	5	2820	1410	403	1950	59	0.178	−6
					Average		0.181	
2-Mercaptobenzoxazole								
Concentration of sulfur and 2-mercaptobenzoxazole 0.33 mole/liter; solvent toluene + ethyl alcohol								
7	2	182	91	29	150	32	0.058	−2
8	6	197	99	44	159	44	0.042	+3
9	8	223	112	64	138	57	0.046	−6
10	12	182	91	64	114	70	0.044	−2
					Average		0.047	
2-Mercaptobenzimidazole								
Concentration of sulfur and 2-mercaptobenzimidazole 0.33 mole/liter; solvent toluene + ethyl alcohol								
11	2	223	113	9	221	8	0.018	+3
12	4	223	113	16	204	14	0.017	−1
13	5	182	92	16	164	17	0.017	−1
14	8	223	113	36	173	32	0.021	−6
15	12	197	100	40	155	40	0.018	−2
					Average		0.018	

From the data given in Table 3 it can be seen that the velocity of the exchange reaction with elementary sulfur decreases in the order:

2-mercaptobenzothiazole > -oxazole > -imidazole.

It is known that a study of the concentration as a function of the apparent velocity constants of isotope exchange reactions, corresponding to the equation $k = -\frac{1}{t} \ln \left(1 - \frac{x}{x_\infty}\right)$, can give valuable information on the mechanism of exchange reactions [1]. When the exchange of sulfur was studied in the systems potassium xanthate-elementary sulfur [2] and sodium diethyldithiocarbamate-elementary sulfur [3] it was found that k is independent of dilution. This is evidence of the fact that the over-all velocity for the process is determined by the velocity of some monomolecular stage in it. Potassium xanthate and sodium diethyldithiocarbamate, the same as the thiono forms of Captax and of the other compounds studied in the present work, contain the C = S bond, and are exchanged by the

general mechanism examined earlier [5,6].

TABLE 2

Exchange Reaction with Elementary Sulfur at 130°

Experiment No.	Duration of Heating (Hrs.)	Activity: In original sulfur	Activity: At Full Exchange	Activity: In the Organic Compound	Activity: In the Sulfur After Exchange	Percent Exchange	k (hr.$^{-1}$)	Difference in Radioactive Isotope Balance (%)
2-Mercaptobenzoxazole								
Concentration of sulfur and 2-mercaptobenzoxazole 0.33 mole/liter; solvent toluene + ethyl alcohol								
1	9	88	44	7	77	16	0.0084	−4
2	19	88	44	14	69	32	0.0087	−6
3	27	88	44	20	64	45	0.0097	−4
					Average		0.009	
2-Mercaptobenzimidazole								
Conditions the same								
4	9	88	44	2	82	4	0.0022	−4
5	19	88	44	3	77	7	0.0018	−9
6	27	88	44	7	75	16	0.0028	0
					Average		0.0023	

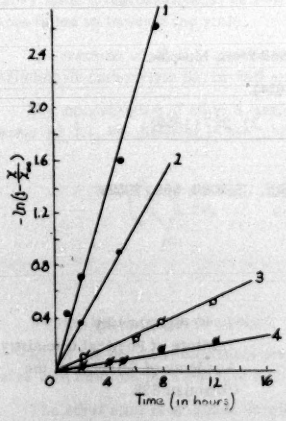

Fig. 1. Relation between the values of $-\ln\left(1-\frac{x}{x_\infty}\right)$ and the time at 150°
1 – 2-mercaptobenzothiazole (C = 0.33 m.),
2 – 2-mercaptobenzothiazole (C = 0.11 m.),
3 – 2-mercaptobenzoxazole (C = 0.33 m.),
4 – 2-mercaptobenzimidazole (C = 0.33 m.).

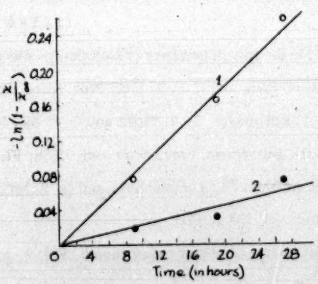

Fig. 2. Relation between the values of $-\ln\left(1-\frac{x}{x_\infty}\right)$ and the time at 130°.
1 – 2-mercaptobenzoxazole (C = 0.33 m.),
2 – 2-mercaptobenzimidazole (C = 0.33 m.)

It could be expected that the exchange velocities for the mercapto-derivatives of thiazole, oxazole and imidazole would also be determined by the velocity of a monomolecular stage. However, the experiments performed with dilute solutions of Captax and sulfur revealed that a 3-fold decrease in the total concentration of the exchanging substances leads to a considerable decrease in the apparent velocity constants for the exchange reaction (Experiments 5 and 6, Table 1). In these experiments $\underline{k} = 0.181$ hr.$^{-1}$, instead of 0.365 hr.$^{-1}$. If the velocity of exchange was determined by the velocity of the bimolecular reaction of Captax with

TABLE 3

Velocity and Energy of Activation Constants of the Exchange Reactions

Compounds Participitating in the Exchange Reaction with Sulfur	k (hr.$^{-1}$)		(kcal/mole)
	130°	155°	
2-Mercaptobenzothiazole	–	0.365	24.0 •
2-Mercaptobenzoxazole	$9 \cdot 10^{-3}$	0.047	27.3
2-Mercaptobenzimidazole	$2 \cdot 10^{-3}$	0.018	34.0

sulfur, then a 3-fold decrease in the concentration of the reagents should have led to a similar reduction in the apparent velocity constants, and k would have been equal to approximately 0.121 hr.$^{-1}$. The differences between the calculated and experimentally found values of k greatly exceed the possible experimental errors and are evidence of the fact that the exchange reaction between Captax and sulfur is not a simple bimolecular reaction. Apparently, the over-all velocity for the process depends on the relation of the commensurate velocities of the separate reaction stages.

The mobility of the sulfur in the 2-mercaptobenzothiazole, -oxazole and -imidazole series decreases in reverse order to the increase in the basicity of the corresponding compounds. 2-Mercaptobenzimidazole possesses the most basic properties, while Captax is the weakest base. Apparently, a relationship can be established between the basicity of corresponding nuclei and the mobility of the attached sulfur.

SUMMARY

1. The kinetics of the reactions for the exchange of elementary sulfur with 2-mercaptobenzothiazole, -oxazole and -imidazole was studied.

2. It was found that the velocity of the indicated reaction decreases in the order: 2-mercaptobenzothiazole > -oxazole > -imidazole.

3. It was found that a 3-fold decrease in the concentration of 2-mercaptobenzothiazole and elementary sulfur results in only a 2-fold reduction in the exchange velocity, which fact is evidence of the stepwise nature of the reaction.

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• The energy of activation values were taken from the studies of E. N. Guryanova [4].

QUINONES

V. SYNTHESIS OF SOME SUBSTITUTED INDOLES AND BENZINDOLES

A. N. Grinev, N. K. Kulbovskaya and A. P. Terentyev

In the previous communications [1, 2] of this series we described the synthesis of a number of benzodifuran and napthofuran derivatives, which were obtained by the reaction of p-quinones ith acetoacetic and benzoylacetic esters. Acetoacetic ester under the influence of ammonia is easily converted into the ethyl ester of β-aminocrotonic acid [3]. The ethyl ester of β-aminocrotonic acid is the nitrogen analog of acetoacetic ester, and like the latter can react with quinones.

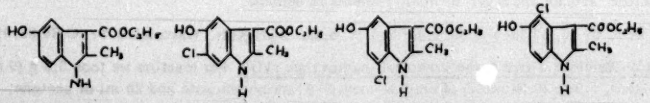
The condensation of p-benzoquinone with ethyl β-aminocrotonate, discovered by Nenitzescu [4], leads to the formation of ethyl 2-methyl-5-hydroxyindole-3-carboxylate. This reaction was further developed in the studies of the English authors [5], who condensed the ethyl β-aminocrotonate with toluquinone, methoxy-p-quinone and hydroxy-p-quinone. Recently it was established by the same authors [6] that the esters of β-amino-α-methylcrotonic and β-amino-β-ethoxyacrylic acids also react with p-benzoquinone.

The purpose of the present study was to prepare compounds belonging to the class of 5-hydroxyindoles and study their properties.

As the result of condensing p-benzoquinone with ethyl β-aminocrotonate we obtained ethyl 2-methyl-5-hydroxyindole-3-carboxylate (I) in 30% yield. Changing the proportions of the reactants and the experimental conditions failed to increase the yield.

The reaction of ethyl β-aminocrotonate with α-naphthoquinone gave the unknown ethyl 2-methyl-5-hydroxybenzindole-3-carboxylate (II) in 56% yield.

The condensation of ethyl β-aminocrotonate with chloro-p-quinone can lead to the formation of a mixture of isomers (III, IV, V), differing in the position of the chlorine atom.



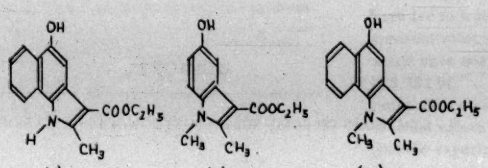
(I) (III) (IV) (V)

We obtained a single compound, characterized by a sharp melting point.

All of the obtained substances are readily oxidized by atmospheric oxygen and form colored compounds when heated with chloroform, alcohol or dichloroethane.

The ethyl ester of β-amino-N-methylcrotonic acid, obtained by the action of methylamine on acetoacetic ester [7], also reacts with p-benzoquinone and α-naphthoquinone.

The ethyl 1,2-dimethyl-5-hydroxyindole-3-carboxylate (VI) and ethyl 1,2-dimethyl-5-hydroxybenzindole-3-carboxylate (VII) obtained by us are more stable to the action of atmospheric oxygen and to heating than the N-unsubstituted 5-hydroxyindoles.



(II) (VI) (VII)

EXPERIMENTAL

Ethyl 2-Methyl-5-hydroxyindole-3-Carboxylate (I). A solution of 27.5 g (0.25 mole) of p-benzoquinone and 65 g (0.5 mole) of β-aminocrotonic ester in 100 ml of acetone was heated under reflux on the water bath for 2 hours. Slow evaporation of acetone from the solution gave the ethyl ester of 2-methyl-5-hydroxyindole-3-carboxylic acid as yellowish crystals in a yield of 18.1 g (30%, based on the quinone). Recrystallization from acetone gave white crystals with m. p. 205°, which coincides with the literature [4].

Ethyl 2-Methyl-5-hydroxybenzindole-3-carboxylate (II). The reaction was run the same as the previous. For reaction there was taken 21 g (0.133 mole) of α-naphthoquinone, 34.4 g (0.266 mole) of ethyl β-aminocrotonate and 100 ml of acetone. Yield of ester was 20 g (56%). White crystals with m. p. 264-265°, readily soluble in acetone and alcohol, difficultly soluble in ether.

Found %: C 71.20, 71.35; H 5.90, 5.77; N 5.12, 4.93. $C_{16}H_{15}O_3N$. Calculated %: C 71.36; H 5.61; N 5.20.

Ethyl Chloro-2-methyl-5-hydroxyindole-3-carboxylate. For reaction there was taken 12 g (0.085 mole) of chloro-p-quinone, 21.9 g (0.17 mole) of ethyl β-aminocrotonate and 60 ml of acetone. The yield of crude product was 3.6 g (16.5%). Crystals with m. p. 213° (from acetone), readily soluble in acetone, alcohol and ether, difficultly soluble in benzine.

Found %: C 56.76, 56.57; H 4.73, 4.92; N 5.52, 5.55; Cl 14.30. $C_{12}H_{12}O_3NCl$. Calculated %: C 56.80; H 4.77; N 5.52; Cl 13.97.

Ethyl 1,2-Dimethyl-5-hydroxyindole-3-carboxylate (VI). The reaction was run under the same conditions as before. We took 1.55 g (0.14 mole) of p-benzoquinone, 4.1 g (0.28 mole) of ethyl N-methyl-β-aminocrotonate and 15 ml of acetone. The yield of ester was 1.6 g (48%). White crystals with m. p. 207-208° (from acetone). Readily soluble in acetone, alcohol and ether, difficultly soluble in benzine.

Found %: C 67.10, 67.11; H 6.69, 6.65; N 61.8, 6.33. $C_{13}H_{15}O_3N$. Calculated %: C 66.93; H 6.48; N 6.00.

Ethyl 1,2-Dimethyl-5-hydroxybenzindole-3-carboxylate (VII). For reaction we took 3.3 g (0.02 mole) of α-naphthoquinone, 5.98 g (0.04 mole) of ethyl N-methyl-β-aminocrotonate and 20 ml of acetone. The yield of crude product was 3 g (51%). Recrystallization from acetone gave white crystals with m. p. 279-280°, soluble in acetone and alcohol, difficultly soluble in ether.

Found %: C 72.08, 71.81; H 6.09, 6.14; N 4.50, 4.59. $C_{17}H_{17}O_3N$. Calculated %: C 72.06; H 6.05; N 4.94.

SUMMARY

The condensation of p-benzoquinone, chloro-p-quinone and α-naphthoquinone with the ethyl esters of β-aminocrotonic and β-amino-N-methylcrotonic acids gave for the first time ethyl 2-methyl-5-hydroxybenzindole-3-carboxylate, ethyl chloro-2-methyl-5-hydroxyindole-3-carboxylate, ethyl 1,2-dimethyl-5-hydroxyindole-3-carboxylate, ethyl 1,2-dimethyl-5-hydroxyindole-3-carboxylate and ethyl 1,2-dimethyl-5-hydroxybenzindole-3-carboxylate.

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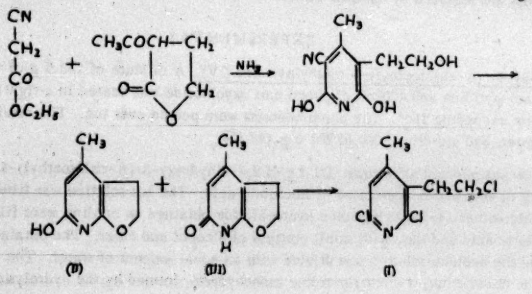
INTERMEDIATE PRODUCT IN THE SYNTHESIS OF TRICHLORO COLLIDINE

M. V. Rubtsov and L. N. Yakhontov

2,6-Di chloro-3-(β-chloroethyl)-4-methylpyridine or trichlorocollidine was obtained by Stevens *, who proceeded from α-acetobutyrolactone, cyanoacetic ester and ammonia in accord with the following scheme.



(II) (III) (I)

We studied the last stage of this scheme in greater detail.

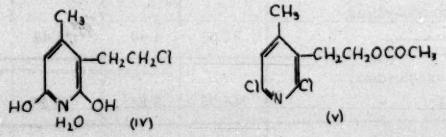
Trichlorocollidine is obtained by heating compounds (II) and (III) with phosphorus oxychloride at 180°. At a lower temperature (120°) Stevens * obtained a substance with m.p. 132.8°, to which he assigned the formula $C_8H_9ONCl_2$, not establishing the positions of the hydroxyl group and chlorine atoms. However, a complete elementary analysis and determination of the water of crystallization revealed that this substance is not dichloromonohydroxycollidine, as postulated by Stevens, but instead is the monohydrate of monochlorodihydroxycollidine (see Table).

The position of the hydroxyl groups and of the chlorine in the monohydrate of monochlorodihydroxycollidine was established on the basis of the following reactions.

The monochlorodihydroxycollidine fails to dehalogenate in the presence of palladium catalyst, which indicates that the halogen is not in the α-position of the pyridine ring.

The heating of the monochlorodihydroxycollidine with excess anhydrous potassium acetate in glacial acetic acid at 175° liberates 1 mole of potassium chloride. The obtained acetyl derivative is halogen-free (Beilstein test). Trichlorocollidine acetylates under similar conditions, forming compound (V).

On the basis of the presented properties and the elementary analysis results the examined compound should be assigned the structure of 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine (IV):

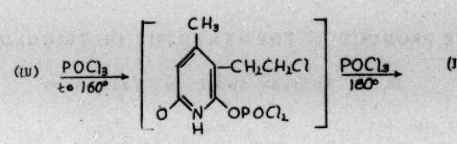


(IV) (V)

When (IV) is heated with alcohol it is readily cyclized to 6-hydroxy-4-methyl-2,3-(2', 3'-dihydrofurano) pyridine (II), while when treated with phosphorus oxychloride at 180° (i.e. under the conditions for obtaining trichlorocollidine) it is transformed into trichlorocollidine.

* J. Am. Chem. Soc. 64, 1093 (1942).

On the basis of the above presented mechanism it is possible to depict the formation of trichlorocollidine in the following manner:



At temperatures not exceeding 160° the dihydrofuran ring is opened, while at higher temperatures (180°) the α, α'-hydroxy groups are replaced by chlorine atoms.

EXPERIMENTAL

2,6-Dihydroxy-3-(β-chloroethyl)-4-methylpyridine (IV). A mixture of 150.0 g of 6-hydroxy-4-methyl-2,3-(2',3'-dihydrofurano)-pyridine and 450 ml of phosphorus oxychloride was heated in a tightly closed bomb for 5 hours at a temperature not exceeding 160°. The bomb contents were poured over ice. The resulting precipitate was filtered, washed with water, and air-dried. Yield 202.0 g (98.5%).

The substance was purified as follows: 22.0 g of 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine was dissolved with heating in 40 ml of concentrated hydrochloric acid. The hot solution was filtered, the crystals of 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine hydrochloride obtained on cooling were filtered, washed with concentrated hydrochloric acid and then with small portions of alcohol and ether. The obtained substance was dissolved in dry acetone, and the acetone solution was diluted with an equal amount of water. The resulting precipitate of 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine monohydrate, formed by the hydrolysis of the hydrochloride, was filtered, washed with water, and dried in a vacuum-desiccator. There was obtained 20.6 g of 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine monohydrate as a white crystalline powder with m.p. 133.5-134°. • The substance is insoluble in water, very difficultly soluble in ether, alcohol, chloroform, acetone and toluene; soluble in pyridine, hot 50% potassium hydroxide solution and in hot concentrated hydrochloric acid, and gives a red coloration with an alcoholic solution of ferric chloride.

Found %: C 46.55, 46.98; H 5.77, 5.70; N 6.73, 6.71; Cl 17.23; H_2O 8.66. •• $C_8H_{10}O_2NCl \cdot H_2O$. Calc.: 46.55%; C 46.76; H 5.81; N 6.81; Cl 17.27; H_2O 8.71.

2,6-Dichloro-3-(β-chloroethyl-4-methylpyridine (Trichlorocollidine) (I). A mixture of 10.0 g of 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine monohydrate and 20 ml of phosphorus oxychloride was heated in a sealed glass tube for 5 hours at 180-190°. The tube contents after cooling were poured over ice. The resulting precipitate was filtered, washed with water, and air-dried. The technical trichlorocollidine (10.8 g) was dissolved in 50 ml of boiling ligroin, the hot solution was filtered, the ligroin was distilled off and the residue was vacuum-distilled at 10 mm. The fraction boiling at 159-161° was collected. The substance crystallized on cooling. M.p. 69-70°.••• Yield 9.3 g (92.8%). The obtained substance failed to depress the melting point when mixed with the trichlorocollidine that was synthesized by the Stevens method from 6-hydroxy-4-methyl-2,3-(2',3'-dihydrofurano) pyridine.

	C	H	Cl	N	H_2O
Calculated for dichloromonohydroxy-collidine	46.60	4.40	34.42	6.79	–
Calculated for monochlorodihydroxy-collidine monohydrate	46.76	5.81	17.27	6.81	8.71
Analysis data according to Stevens	46.89	4.81	–	–	–
Data of the Microanalysis Laboratory of All-Union Scientific-Research Chemical-Pharmaceutical Institute	46.55 46.98	5.77 5.70	17.23 17.30	6.73 6.71	} 8.66

• Stevens gives a m.p. of 132.8° for the compound to which he assigns the formula of dichloromonohydroxycollidine.

•• When heated in a vacuum-pistolet at 140°.

••• Stevens gives for trichlorocollidine a m.p. of 69-70° and b.p. 160-161° (10 mm).

SUMMARY

1. It was shown that the intermediate substance formed in the preparation of trichlorocollidine is 2,6-dihydroxy-3-(β-chloroethyl)-4-methylpyridine.

2. The mechanism for the formation of trichlorocollidine from 4-methyl-6-hydroxy-2,3-(2',3'-dihydrofurano) pyridine and its oxo-isomer was elucidated.

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S. Ordzhonikidze

α-SUBSTITUTED α-AMINO ACIDS

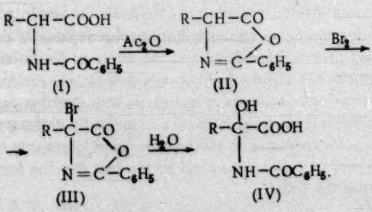
I. SYNTHESIS AND PROPERTIES OF THE SIMPLER α-HYDROXY-α-ACYLAMINOCARBOXYLIC ACIDS

E. S. Chaman and M. M. Shemyakin

It has been known for a comparatively long time that the α-hydroxy-α-amino acids are also a subgroup of natural-occurring amino acids. Thus, it was established with considerable certainty that the residues of two of the α-hydroxy-α-amino acids (α-hydroxy-α-alanine and α-hydroxyvaline) are present in the peptide portion of almost all of the ergot alkaloids (rye fungus alkaloids) [1, 2]. The theory was also expressed that one of the components of the antibiotic lycomarasmine is α-hydroxy-α-alanine and that the high antibiotic activity shown by lycomarasmine is specifically due to the presence of this amino acid residue [3]. The whole class of α-hydroxy-α-amino acids has as yet been very slightly studied—methods for the synthesis of these compounds are absent and their properties and transformations have hardly been studied; in addition, the great instability of the α-hydroxy-α-amino acids renders their isolation from natural-occurring products extremely difficult, and also their synthesis and study. In the meantime, these compounds are of considerable interest since they are the structural elements of a number of important natural-occurring substances.

We have now found a way to synthesize the N-acylated derivatives of α-hydroxy-α-amino acids and were able to synthesize for the first time several of the simpler members of this class of compounds; namely, the N-benzoyl derivatives of hydroxyglycine, α-hydroxy-α-alanine and α-hydroxy-α-aminobutyric acid. Our method permits starting from readily available N-acylated derivatives of α-amino acids, whereupon the introduction of the hydroxyl group at the α-carbon of the latter is accomplished in three steps—first the starting α-benzoylamino acid (I) is transformed by heating with acetic anhydride into the corresponding oxazolinone (II); then this compound is brominated in dry dichloroethane to the 4-bromooxazolinone derivative (III), which, finally, by treatment with water is converted directly into the α-hydroxy-α-benzoylaminocarboxylic acid (IV). If instead of water, an alcohol solution of a sodium alcoholate is taken, then the ester of the corresponding α-alkoxy-α-acylaminocarboxylic acid is formed.

As a result, the method found by us for the synthesis of N-acylated α-hydroxy-α-amino acids is quite simple as regards execution. This method can be used for introducing not only the hydroxyl group in the α-position of α-acylamino acids, but also other substituents (alkoxy groups, amino groups, etc.).



The first step of the synthesis (preparation of oxazolinones) was usually accomplished by us under the conditions given in the literature; consequently, a more detailed examination of this step here is considered superfluous.

As regards the second step—the bromination of oxazolinones in the 4-position—then this earlier unknown reaction deserves more detailed illumination. In the case of a simpler oxazolinone (2-phenyloxazolin-5-one) this reaction proceeds very easily even at low temperature; however, the bromination of 4-alkyl-substituted oxazolinones of type (II) is somewhat more difficult and requires a slightly elevated temperature for its realization. It should also be mentioned that the hydrogen bromide, formed during the bromination, usually reacts immediately

with the still unchanged oxazolinone, transforming it into the hydrobromide of the oxazolinone (or the acid bromide of the corresponding α-acylamino acid), which is either completely or partially precipitated from solution; thus being deprived of the possibility of reacting further with the bromine. In the case of the simpler 2-phenyloxazolin-5-one its hydrobromide is completely precipitated from solution, and consequently only one half of the taken amount of oxazolinone is exposed to bromination (instead of 1 mole of bromine, only 0.5 mole is consumed). The bromination of 4-alkyl-substituted oxazolinones is accompanied by a lesser precipitation of their hydrobromides, as a result of which the amount of oxazolinones exposed to bromination is correspondingly increased.

The replacement of the bromine atom in the bromooxazolinone by the hydroxyl group and the opening of the oxazolinone ring (third or last step of the synthesis) were realized simultaneously in the cases studied by us and proceeded with great ease when a dichloroethane solution of the bromooxazolinone was stirred with water; previous isolation and purification of the bromooxazolinone was needless.

We should dwell briefly on some of the properties of the N-benzoylated α-hydroxy-α-aminocarboxylic acids obtained by us. They all are colorless crystalline substances, difficultly soluble in water and readily soluble in many of the organic solvents. One of the most characteristic properties of these compounds is the extreme ease with which they suffer hydrolysis to the corresponding keto acids and benzamide in accord with the following general scheme:

$$RC(OH)(NHCOC_6H_5)COOH \longrightarrow RCOCOOH + C_6H_5CONH_2.$$

This reaction proceeds with especial ease at solution pH values above 7. In the presence of an aqueous solution of sodium bicarbonate the reaction is already slowly realized in the cold, while when boiled, the reaction is complete in a matter of 2-3 minutes. The hydrolysis proceeds with somewhat more difficulty in acid medium. Thus, N-benzoylhydroxyglycine at room temperature in the presence of a 5% aqueous-alcohol solution of hydrogen chloride is practically unaffected, while the hydrolysis of the homologs of N-benzoylhydroxyglycine under these conditions is very slight. Only on heating does the acid hydrolysis of all of the α-hydroxy-α-acylamino acids proceed with comparative ease.

In conclusion it should be mentioned that a comparison of the properties of the α-hydroxy-α-acylamino acids synthesized by us with the properties of the ergot alkaloids, and also of the antibiotic lycomarasmine, confirms the validity of the statements made in the literature that the radical of α-hydroxy-α-amino acids are present in the molecules of these natural-occurring compounds. Up to now these opinions were based only on indirect experimental data and analogies, since the synthesis of the individual α-hydroxy-α-acylamino acids had not been realized before and their properties had remained unstudied. It is essential that the method discovered by us for the synthesis of N-acyl-α-hydroxy-α-amino acids will make it possible to approach the synthesis of compounds that are close in their structure to the ergot alkaloids, and first of all those analogs that constitute the N-lysergyl-α-hydroxy-α-amino acids.

Finally, it is expedient that we turn our attention to still another matter. It is known that at times in the hydrolysis of peptides and albumins the presence of α-keto acids is manifested in the hydrolysis products, the formation of which is usually associated with the presence of β-hydroxy-α-amino acid radicals in the original compounds; these residues, as the result of dehydration and then hydrolysis, are capable of transformation into the corresponding α-keto acids. However, the fact must be considered that the origin of the latter can also be associated with the presence in the hydrolyzed peptides and albumins of not only β-hydroxy- residues, but also of α-hydroxy-α-amino acid residues, the latter being capable of undergoing hydrolysis with extreme ease; consequently, when α-keto acids are present in the hydrolysis products it becomes necessary to specially delineate each time the question as to the character of the hydroxyamino acids appearing as their predecessors. Probably the α-hydroxy-α-amino acids can be easily distinguished from the β-hydroxy-α-amino acids by the fact that the former should decompose to the α-keto acids with much greater ease than the latter.

EXPERIMENTAL

1. Preparation of Oxazolinones

2-Phenyloxazolin-5-one was obtained under the earlier described conditions by heating hippuric acid with acetic anhydride [4].

4-Methyl-2-phenyloxazolin-5-one, described earlier [5], was obtained by heating benzoyl-α-alanine with a 5-fold amount of acetic anhydride until the precipitate dissolved (bath temperature 70-80°, duration of heating about

30 minutes). After distilling off the acetic anhydride in vacuo (bath temperature not above 40°) the oxazolinone distilled at 108-112° (2-3 mm). Yield about 80%.

4-Ethyl-2-phenyloxazolin-5-one, previously unknown in the literature, was obtained in 90% yield under the same conditions as for the previous oxazolinone. 4-Ethyl-2-phenyloxazolin-5-one distills at 114-117° (2-3 mm). After recrystallization from petroleum ether in the presence of several drops of acetic anhydride the substance melts at 48-50°.

Found %: C 69.52; H 5.86; N 7.71. $C_{11}H_{11}O_2N$. Calculated %: C 69.82; H 5.86; N 7.40.

The obtained oxazolinone was characterized as the amide of α-benzoylaminobutyric acid by treatment with aqueous ammonia; m.p. 198-200° (from alcohol).

Found %: C 63.99; H 6.82. $C_{11}H_{14}O_2N_2$. Calculated %: C 64.06; H 6.83.

2. Preparation of N-Benzoyl- α-hydroxy-α-amino Acids

N-Benzoylhydroxyglycine. To a solution of 12.8 g of 2-phenyloxazolin-5-one in 80 ml of dry dichloroethane at 4-7° was added dropwise a solution of 6.9 g of bromine in 20 ml of dichloroethane. The crystals of 2-phenyloxazolin-5-one hydrobromide formed during the time of bromine addition were filtered, washed with dichloroethane, and then dissolved in 5% sodium hydroxide solution. Acidification of the alkaline solution gave 5.7 g (40%) of hippuric acid.

The dichloroethane solution was vigorously stirred at room temperature for 2-3 hours with 100 ml of water. The obtained crystals of N-benzoylhydroxyglycine were filtered and washed with water. The substance was recrystallized by dissolving in the minimum amount of dioxane and adding with rubbing a small amount of chloroform until crystallization began. N-Benzoylhydroxyglycine begins to darken around 146° and melts at 200-202°. Yield 5.5 g (35%).

Found %: C 55.61; H 4.78; N 7.43. Equiv. (titration) 198. $C_9H_9O_4N$. Calculated %: C 55.46; H 4.66; N 7.18. Equiv. 195.

Ethyl N-Benzoylethoxyglycinate. Five grams of 2-phenyloxazolin-5-one was brominated as described above, and after removing the hydrobromide of the original oxazolinone, to the obtained dichloroethane solution at room temperature was added an alcohol solution of 4.2 g of sodium ethylate. The following day the solution was neutralized with glacial acetic acid and, having added water, the dichloroethane layer was separated, washed with water, sodium bicarbonate solution and again with water, then dried over sodium sulfate and, finally, the dichloroethane was distilled in vacuo, after which the oily residue was vacuum-distilled at 3-4 mm. At 75° several drops of ethyl benzoate distilled, and then a viscous, rapidly crystallizing oil distilled at 130-135°. The obtained ethyl N-benzoylethoxyglycinate was recrystallized several times from aqueous alcohol or from aqueous dioxane. The substance crystallizes as white needles with m.p. 69-71°.

Found %: C 62.15; H 6.74; N 5.47. $C_{13}H_{17}O_4N$. Calculated %: C 62.13; H 6.82; N 5.57.

N-Benzoyl-α-hydroxy-α-alanine. To a solution of 6.9 g of 4-methyl-2-phenyloxazolin-5-one in 50 ml of dry dichloroethane at 10-12° was added dropwise a solution of 3.5 g of bromine in 10 ml of dichloroethane. The hydrobromide of the original oxazolinone, formed during the time of bromine addition, was filtered, washed with dichloroethane, and dissolved in 5% sodium hydroxide solution. Acidification of the alkaline solution gave a 2.5 g (33%) of N-benzoyl-α-alanine.

The dichloroethane solution was vigorously stirred with 50 ml of water at room temperature for 2 hours and let stand overnight. The obtained N-benzoyl-α-hydroxy-α-alanine was filtered and washed with water. Yield 2.2 g (27%); m.p. 100-102°. The substance was recrystallized by dissolving in the minimum amount of dioxane and adding with rubbing a small amount of chloroform until crystallization began. The pure N-benzoyl-α-hydroxy-α-alanine melts at 103-105°.

Found %: C 57.21; H 5.37; N 6.73. Equiv. (titration) 212. $C_{10}H_{11}O_4N$. Calculated %: C 57.41; H 5.30; N 6.69. Equiv. 209.

N-Benzoyl-α-hydroxy-α-aminobutyric Acid. To a solution of 7.7 g of 4-ethyl-2-phenyloxazolin-5-one in 45 ml of dry dichloroethane at 16-20° was added dropwise a solution of 6.5 g of bromine in 15 ml of dichloroethane. The hydrobromide of the original oxazolinone, separating at the beginning of reaction, gradually dissolved with further addition of bromine. At the end of reaction 50 ml of water was added to the reaction mass and the mixture was vigorously stirred at room temperature for 3 hours. The obtained crystals of N-benzoyl-α-hydroxy-α-aminobutyric acid were filtered and washed with water. Yield 2.05 g; m.p. 93-98°. The dichloroethane solution was separated from the water layer, dried over sodium sulfate; the dichloroethane was removed in vacuo and ether was added to the

residue, as a result of which another 0.35 g of substance was obtained. The total yield of N-benzoyl-α-hydroxy-α-aminobutyric acid was 2.4 g (26%). The substance was purified by dissolving in the minimum amount of dioxane and then adding chloroform with rubbing until crystallization began. After two recrystallizations the hydroxyamino acid has m.p. 98-99°.

Found %: C 59.31; H 5.94. $C_{11}H_{13}O_4N$. Calculated %: C 59.18; H 5.91.

From the ether mother liquor after removing the ether there was obtained 2 g (24%) of α-benzoylaminobutyric acid by dissolving the residue in aqueous sodium bicarbonate solution and acidifying the thus obtained solution.

3. Hydrolysis of α-Hydroxy-α-benzoylamino Acids

a) N-Benzoylhydroxyglycine was heated with an 8% sodium bicarbonate solution for 2-3 minutes, the mixture cooled, and the obtained benzamide filtered; m.p. 129-130° (from water). The filtrate was divided into two portions. The treatment of one portion with a solution of aminoguanidine in 50% acetic acid gave the aminoguanidine derivative of glyoxylic acid, which after recrystallization from water melted with decomposition at 141-142°. Treatment of the other filtrate portion with a solution of 2,4-dinitrophenylhydrazine in 5% hydrochloric acid gave the 2,4-dinitrophenylhydrazone of glyoxylic acid with m.p. 188-190° (from aqueous alcohol).

N-Benzoylhydroxyglycine was heated for 30 minutes with a 5% aqueous-alcohol solution of hydrogen chloride and after cooling the glyoxylic acid was isolated from the solution as the 2,4-dinitrophenylhydrazone. The hydrolysis of N-benzoylhydroxyglycine in a 5% aqueous-alcohol solution of hydrogen chloride fails to proceed at room temperature.

b) N-Benzoyl-α-hydroxy-α-alanine was heated with an 8% sodium bicarbonate solution and after cooling the obtained benzamide was filtered, while from the solution pyrotartaric acid was isolated as the 2,4-dinitrophenylhydrazone; m.p. 212-213° (from a mixture of acetic acid and alcohol).

N-Benzoyl-α-hydroxy-α-alanine was heated for 30 minutes with a 5% aqueous-alcohol solution of hydrogen chloride. After cooling, the pyrotartaric acid was isolated from the solution as the 2,4-dinitrophenylhydrazone. At room temperature the acid hydrolysis of N-benzoyl-α-hydroxy-α-alanine proceeds very slowly.

c) N-Benzoyl-α-hydroxy-α-aminobutyric acid was hydrolyzed under the conditions described in 3b for the hydrolysis of N-benzoyl-α-hydroxy-α-alanine. After hydrolysis with sodium bicarbonate solution benzamide and the 2,4-dinitrophenylhydrazone of α-ketobutyric acid (m.p. 195-197°) were isolated, and after acid hydrolysis only the latter compound.

SUMMARY

A method for the synthesis of N-acylated α-hydroxy-α-amino acids was found and the simpler members of this class of compounds were synthesized; namely, the N-benzoyl derivatives of hydroxyglycine, α-hydroxy-α-alanine and α-hydroxy-α-aminobutyric acid. It was shown that one of the most characteristic properties of these compounds is the extreme ease with which they hydrolyze to the corresponding α-keto acids and benzamide.

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* T. p. = Translation pagination.

REACTION OF β-CHLOROVINYL KETONES WITH PHENYL AZIDE

N. K. Kochetkov

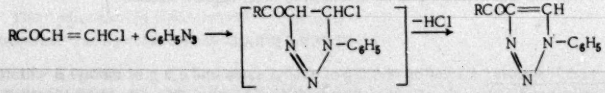
Recently it was shown in the work of Nesmeyanov and Kochetkov that β-chlorovinyl ketones react smoothly with diazomethane and diazoacetic ester, forming ketones of the pyrazole series [1]. Proceeding from the known analogy in the behavior of organic azides with aliphatic diazo compounds, already indicated by Dimroth [2], we studied the reaction of β-chlorovinyl ketones with phenyl azide, one of the more typical azide representatives. In a previous communication [3] it was shown that phenyl azide reacts with methyl β-chlorovinyl ketone, forming 1-phenyl-4-acetyl-1,2,3-triazole. We can now communicate on the details of this work and on the extension of this synthesis to other β-chlorovinyl ketones.

It was revealed that the reaction found by us is quite general in character and can serve as a method for the synthesis of ketones of the triazole series, which up to now have been difficultly available compounds [4-6], but which deserve attention in connection with the synthesis development of other triazole derivatives on their basis.

The condensation of β-chlorovinyl ketones with phenyl azide proceeds under heating of equimolar amounts of both reactants in boiling benzene for 10-15 hours.

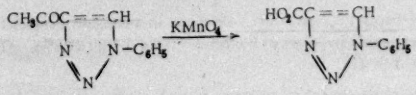
The yields of the 1-phenyl-4-acetyl triazoles vary in the limits of 20-60%, in which connection a decrease in yield can be noted with increase in radical size. Attempts to achieve better results by prolonging the reaction time or by using a higher boiling solvent proved unsuccessful. Only an increase in the amount of tarry impurities could be observed, which made the isolation of the reaction product extremely difficult. The use of excess phenyl azide also failed to increase the yields.

It is most probable that this reaction proceeds through preliminary addition of the phenyl azide to the double bond of the β-chlorovinyl ketone with subsequent cleavage of the elements of hydrogen chloride, which is facilitated by the fact that this leads to the formation of a heterocyclic system, possessing aromatic character. Thus, the mechanism for the reaction can be depicted by the scheme



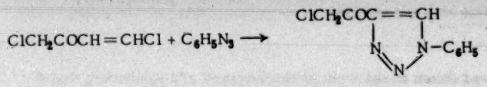
The reaction of β-chlorovinyl ketones with aliphatic diazo compounds was explained in a similar manner [1]. The condensation with phenyl azide is different only in that in this case the evolved hydrogen chloride fails to combine with the formed nitrogen-containing heterocycle, whereas in the reaction with diazomethane the hydrochloride of the pyrazole ketone is obtained. The explanation for this difference is to be sought in the lower basicity of the triazole, a difference that has repeatedly been noted in the literature.

The condensation of phenyl azide with alkyl β-chlorovinyl ketones can proceed in two directions, leading to the formation of 1-phenyl-4-acyl triazoles and 1-phenyl-5-acyl triazoles or a mixture of both isomers. Actually, in all of our studied cases only one substance was formed. The structure of the obtained compounds was judged on the basis of the results obtained for the oxidation of the first member of the series; namely, the phenylacetyltriazole. Oxidation of this compound with permanganate gave 1-phenyltriazole-4-carboxylic acid



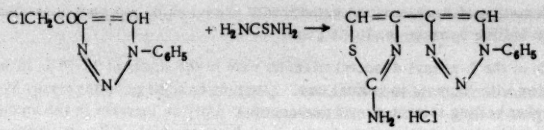
This indicates that the obtained compounds are actually 1-phenyl-4-acyl triazoles. As a result, in the investigated reaction the usual reciprocal orientation of the α, β-unsaturated carbonyl compound and the phenyl azide is retained (for example, see [7]), despite the presence of a chlorine atom at the β-carbon atom.

In addition to the alkyl β-chlorovinyl ketones (methyl, propyl and isobutyl β-chlorovinyl ketones), we also studied this reaction for the case of chloromethyl β-chlorovinyl ketone. It was revealed that in this case the reaction proceeds by the usual scheme, and the corresponding α-chloro ketone of the triazole series is formed in about 60%:



The obtained compound is of especial interest for developing the synthesis of new triazole derivatives, since the high reactivity of α-chloro ketones is generally known and, in particular, is widely used for the synthesis of heterocyclic compounds.

For the purpose of verifying the possibility of synthesizing some new compounds, containing two different heterocyclic rings, on the basis of the obtained chloro ketone, and also for confirming the structure of the chloro ketone, we studied its reaction with thiourea. It was revealed that when the two reactants are heated in anhydrous alcohol the condensation proceeds smoothly and a compound, containing both the thiazole and triazole rings, is obtained in extremely high yield:



Treatment of the hydrochloride obtained in the condensation with alkali permits easy isolation of the free base. Both the hydrochloride of 1-phenyl-4-(2-amino-4-thiazolyl)-1,2,3-triazole and the free base are stable high-melting compounds, which crystallize with one mole of water.

The present investigation shows that the reaction of β-chlorovinyl ketones with phenyl azide is quite general in character and may prove useful for the synthesis of a number of difficultly available triazole compounds. There is reason to believe that the reaction can also be extended to other organic azides.

EXPERIMENTAL

1-Phenyl-4-acetyltriazole. A solution of 3.5 g of phenyl azide and 3.0 g of methyl β-chlorovinyl ketone in 10 ml of benzene was heated under reflux on the water bath for 10 hours. The solvent and a small amount of unreacted material were vacuum-distilled on the water bath. The crystallization of the residue was both rapid and complete, the crystals were pressed on porous plate, and then recrystallized from aqueous alcohol. Scales of mother-of-pearl luster with m.p. 108-109°. Yield 2.1 g (38%).

Found %: C 64.07, 64.02; H 4.88, 4.76. $C_{10}H_9ON_3$. Calculated %: C 64.19; H 4.81.

1-Phenyl-4-acetyltriazole is readily soluble in acetone and hot alcohol, difficultly soluble in water. Iodoform is liberated when the compound is treated with alkaline iodine solution.

The semicarbazone was obtained in aqueous methyl alcohol and was recrystallized from alcohol. Colorless crystals with m.p. 222-223°.

Found %: N 34.29, 34.13. $C_{11}H_{12}ON_6$. Calculated %: N 34.40.

1-Phenyl-4-butyl-1,2,3-triazole. Obtained in analogous manner from 6.5 g of propyl β-chlorovinyl ketone and 7.0 g of phenyl azide in 25 ml of benzene. Yield 3.1 g (29.2%). After recrystallization from alcohol—snow-white needles with m.p. 109-110°.

Found %: N 19.43, 19.47. $C_{12}H_{13}ON_3$. Calculated %: N 19.52.

1-Phenyl-4-butyryltriazole is readily soluble in hot alcohol, difficultly soluble in cold alcohol, insoluble in water.

1-Phenyl-4-isovaleryl-1,2,3-triazole. Obtained in analogous manner from 2.0 g of isobutyl β-chlorovinyl ketone and 4.0 g of phenyl azide in 20 ml of benzene. When the solvent is removed by vacuum distillation, a considerable amount of unreacted substances is also distilled. The residue in the flask fails to crystallize completely, and only after prolonged ice-cooling. Recrystallization from aqueous alcohol gave fine needles with m.p. 90.5-91°. Yield 0.63 g (21%).

Found %: N 18.43, 18.64. $C_{13}H_{15}ON_3$. Calculated %: N 18.33.

1-Phenyl-4-isovaleryltriazole is readily soluble in alcohol and acetone and insoluble in water.

Oxidation of 1-Phenyl-4-acetyltriazole. A mixture of 0.3 g of the substance and 20 ml of a 3% sodium hydroxide solution was heated until the triazole melted, after which a saturated solution of potassium permanganate was added and then slightly later 0.3 g of finely ground crystalline permanganate. The mixture was heated on the water bath, and then on the gauze until the solution was completely decolorized. The manganese dioxide was filtered and washed with water, while the filtrate and wash liquors were extracted with ether. The aqueous layer was acidified with 5% hydrochloric acid and extracted three times with ether; the ether was removed from the ether extracts after drying; the crystalline residue was recrystallized from water and dried at 100°. Colorless needles with m.p. 149-150°.

Literature for 1-phenyltriazole-4-carboxylic acid [8]: m.p. 151°.

1-Phenyl-4-(chloroacetyl)-1,2,3-triazole. A solution of 5.0 g of chloromethyl β-chlorovinyl ketone and 6.0 g of phenyl azide in 20 ml of benzene was heated for 6 hours. The precipitate obtained on cooling was filtered and recrystallized from benzene. Colorless needles with m.p. 154-155°. Yield 4.1 g (61%).

Found %: N 19.07, 18.93. $C_{10}H_8ON_3Cl$. Calculated %: N 18.91.

1-Phenyl-4-(chloroacetyl)-triazole is readily soluble in hot benzene and alcohol, difficultly soluble in cold benzene, insoluble in water.

Reaction of 1-Phenyl-4-(chloroacetyl)-1,2,3-triazole with Thiourea. A solution of 0.20 g of 1-phenyl-4-(chloroacetyl)-triazole and 0.10 g of thiourea in 10 ml of anhydrous alcohol was heated on the water bath for 6 hours. The crystals obtained on cooling were filtered, dried, and recrystallized from anhydrous alcohol. Colorless lustrous scales with m.p. 233-235° (with decompn.). Yield 0.25 g (96%).

Found %: C 44.44, 44.55; H 4.12, 3.97. $C_{11}H_{10}N_5SCl \cdot H_2O$. Calculated %: C 44.40; H 4.07.

The hydrochloride is soluble in water and hot alcohol, insoluble in ether.

Free Base. The hydrochloride was dissolved in boiling water and treated with a 10% sodium hydroxide solution. The obtained precipitate was filtered and recrystallized from aqueous alcohol. Fine colorless crystals with m.p. 174-175°.

Found %: N 26.42, 26.44. $C_{11}H_9N_5S \cdot H_2O$. Calculated %: N 26.80.

The compound is readily soluble in alcohol and ether, practically insoluble in cold water.

SUMMARY

1. The reaction of β-chlorovinyl ketones with phenyl azide yields 1-phenyl-4-acyl-1,2,3-triazoles. This reaction can serve as a convenient synthesis method for these compounds.

2. The structure of the obtained triazole ketones was shown by oxidation of the first member of the series, which led to 1-phenyltriazole-4-carboxylic acid.

3. The reaction of 1-phenyl-4-(chloroacetyl)-triazole with thiourea yields compounds that simultaneously contain both the thiazole and the triazole rings.

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A NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

XX. ADDITION OF PARTIAL ESTERS OF PHOSPHORUS ACIDS TO ESTERS OF ISOCYANIC ACID

A. N. Pudovik and A. V. Kuznetsova

Taking into consideration the great reactivity of isocyanic acid esters and their manifested tendency toward different addition reactions we decided, in developing and expanding on the investigations made by one of us in the last several years on the development of a new method for the synthesis of esters of phosphinic and thiophosphinic acids [1], to effect the addition of the partial esters of phosphorous, thiophosphorous and dithiophosphoric acids to the esters of isocyanic acid. In performing these experiments we used the conditions of the addition reaction method developed by us earlier and described in previous papers.

In the absence of catalysts the reaction of methyl isocyanate with the dialkylphosphorous and dialkylthiophosphorous acids is very slow, while in the presence of sodium alcoholates the reaction proceeds rapidly and vigorously with considerable heat evolution. The temperature of the reaction mixtures rises to 40-50°.

Phenyl isocyanate is more active; dimethylthiophosphorous acid adds to it in the absence of catalyst. Without catalyst the addition of the other acids proceeds very slowly and incompletely; together with the addition product there is also formed a small amount of diphenylurea as the result of phenyl isocyanate hydrolysis. In the presence of sodium ethylate the reaction proceeds very vigorously.

Only the dimethyl esters of anilinophosphono- and anilinothiophosphonoformic acids were obtained pure and in sufficiently good yields. The crystallization of the higher esters proceeds very slowly and the obtained products are difficult to purify. The addition reaction proceeds in accord with the scheme:

$$(RO)_2POH + RONa \rightleftharpoons (RO)_2PONa + ROH.$$

$$R'-N=C=O + (RO)_2PONa \rightarrow R'-N=\underset{\underset{(RO)_2P=O}{|}}{C}-ONa \xrightarrow{(RO)_2POH}$$

$$\longrightarrow R'-NH-CO-\overset{\overset{O}{\parallel}}{P}(OR)_2 + (RO)_2PONa, \text{ etc.}$$

where $R = CH_3, C_2H_5, C_4H_9$ and $R' = CH_3, C_6H_5$.

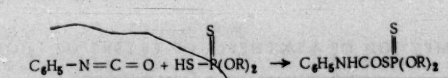
Due to the unshared electron pair found at the phosphorus atom the addition of the sodium diethylphosphite or diethylthiophosphite proceeds first at the carbonyl group of the isocyanic acid ester, after which the addition product rearranges into the substituted amine (preferred to amide) of the dialkylphosphono- or dialkylthiophosphonoformic acid. The addition products are characterized in the Table.

The synthesized esters of methyl- and anilinophosphono- and anilinothiophosphonoformic acids are readily soluble in alcohol, ether, benzene and dioxane. Some of them are soluble in water; in aqueous solution they are quite stable.

To prove the structure of the obtained products one of them—the dimethyl ester of anilinophosphonoformic acid—was prepared by the method of A. E. Arbuzov. The mixed melting point failed to be depressed.

In conclusion we ran a number of experiments on the addition of the partial esters of diethyldithiophosphoric acid to the phenyl and methyl esters of isocyanic acid. As the studies showed [2], and also [3], the partial esters of the dialkyldithiophosphoric acids are exceedingly reactive substances, easily adding to unsaturated hydrocarbons and their various derivatives. The addition of dimethyldithiophosphoric and diethyldithiophosphoric acids to phenyl

isocyanate proceeds very easily. When the reactants are poured together the temperature of the reaction mixture quickly rises to 60-70°.



Formula	Boiling Point at Pressure (mm)	Melting Point	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calculated	Analysis for Phosphorus and Sulfur (in %) Found	Analysis for Phosphorus and Sulfur (in %) Calculated	Yield (in %)
$CH_3NHCOP(=O)(OCH_3)_2$	135-137 (2)	–	1.4585	1.2929	35.27	35.13	P 18.44, 18.43	P 18.57	45
$CH_3NHCOP(=O)(OC_2H_5)_2$	142 (3)	–	1.4525	1.1800	44.62	44.38	P 15.72, 15.99	P 15.90	60
$CH_3NHCOP(=O)(OC_4H_9\text{-}n)_2$	182-183 (9)	–	1.4448	1.0591	63.05	62.86	P 12.32, 12.08	P 12.35	49
$CH_3NHCOP(=O)(OC_4H_9\text{-}iso)_2$	162 (7)	39-40°	–	–	–	–	P 12.37	P 12.35	58
$CH_3NHCOP(=S)(OCH_3)_2$	144-145 (11)	–	1.5118	1.2873	42.65	42.62	P 16.79, 16.96	P 16.93	54
$CH_3NHCOP(=S)(OC_2H_5)_2$	139 (5)	36-37	–	–	–	–	P 14.64, 14.46	P 14.69	55
$CH_3NHCOP(=S)(OC_4H_9\text{-}n)_2$	172-173 (9)	–	1.4838	1.0821	70.56	70.33	P 11.24, 11.27	P 11.61	37
$C_6H_5NHCOP(=O)(OCH_3)_2$	–	103	–	–	–	–	P 13.70, 13.56	P 13.54	95
$C_6H_5NHCOP(=S)(OCH_3)_2$	–	107-108	–	–	–	–	P 12.88, 12.77	P 12.66	67
$C_6H_5NHCOSP(=S)(OCH_3)_2$	–	93	–	–	–	–	P 11.32, 11.16 S 23.16, 23.02	P 11.19 S 23.10	66
$C_6H_5NHCOSP(=S)(OC_2H_5)_2$	–	56	–	–	–	–	P 9.65, 9.92 S 20.86, 20.63	P 10.16 S 20.98	82

The yields of the addition products are 70-80%. The products are readily soluble in alcohol, dioxane and benzene, and partially soluble in water. The dithiophosphoric acid esters are hydrolyzed when saponified with hydrochloric acid. Aniline hydrochloride was isolated from the saponification products.

The testing of the synthesized compounds for toxicity against the grain weevil revealed that they are extremely weak insecticides.

EXPERIMENTAL

Addition of Dialkylphosphorous, Dialkylthiophosphorous and Dialkyldithiophosphoric Esters to Isocyanic Acid Esters. The reactions were run by the general method. Equimolar mixtures of isocyanic acid esters and the partial esters of phosphorous, thiophosphorous or dithiophosphoric acid, placed in a small round-bottomed flask, were heated under reflux on the water bath for 20-40 minutes with or without the addition of dry sodium alcoholate. The obtained addition products were either vacuum-distilled or recrystallized. The constants of the obtained products, the yields, the molecular refraction values and the analysis data for the amount of phosphorus and sulfur are given in the Table.

Reaction of Trimethyl Phosphite with the Acid Chloride of Phenylcarbamic Acid. The reaction was run with 12 g of trimethyl phosphite and 7 g of phenylcarbamoyl chloride; the reaction mixture heated up and methyl chloride was evolved. The yield of the dimethyl ester of anilinophosphonoformic acid with m.p. 102-103° was 10 g. The mixed melting point with the product obtained by the addition of dimethylphosphorous acid to phenyl isocyanate failed to be depressed.

SUMMARY

1. It was found that the dialkylphosphorous and dialkylthiophosphorous acids add to isocyanic acid esters with the formation of the substituted amines (preferred to amides) of the dialkylphosphonoformic acid.

2. The addition of dimethylphosphorous, diethylphosphorous, di-n-butylphosphorous and diisobutylphosphorous acids, and their thio analogs, to methyl isocyanate was accomplished, as well as the addition of dimethylphosphorous and dimethylthiophosphorous acids to phenyl isocyanate.

3. It was shown that the partial esters of dithiophosphoric acids add to phenyl isocyanate with the formation of phenylcarbamoyldialkyldithiophosphoric acids.

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* T. p. = C. B. Translation pagination.

THE SYNTHESIS AND TRANSFORMATIONS OF SOME DI-2-THIENYLMETHANE DERIVATIVES

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Di-2-thienylmethane (I) is a comparatively available compound, being formed in the chloromethylation of thiophene [1] or in the reaction of thiophene with formaldehyde in the presence of hydrofluoric acid [2]. Retaining two unsubstituted α-hydrogen atoms, (I) is capable of giving the diketone (II) when acetylated [2]; as is known, the unsubstituted thiophene under similar conditions forms only the monoacetyl derivative. Compounds having two (or one) functional groups at the terminal carbon atoms of the di-2-thienylmethane, or their isomers, which could be synthesized by replacing the hydrogen atoms in the latter with the methylene group, are of interest as possible starting materials for the preparation of long open-chain derivatives by the method of desulfurization. For this purpose we made a study of the metalation of di-2-thienylmethane and of the transformations of the resulting products. Since the α-hydrogen atom in thiophene and its homologs is easily substituted by sodium or lithium [3], it could be assumed that under certain conditions the dimetallic derivatives of structure (IV) would be obtained from (I); in addition it is known that the compounds, formed in the reaction of diphenylmethane with the alkali metals, originate as the result of hydrogen displacement from the methylene group.

The experiments on the transmetalation of di-2-thienylmethane by means of enriched sodium amalgam and butyl bromide or bromobenzene failed to give sufficiently clear results, although Schick and Hartough [3] were able to obtain 2-thienylsodium in good yield by this method. In contrast, the metalation of (I) with n-butyllithium goes almost to completion; this can be judged by the yields of the compounds formed from the lithium derivatives. Thus, for example, the reaction product from equimolar amounts of butyllithium and di-2-thienylmethane gives with ethylene oxide the monohydric alcohol of composition $C_{11}H_{12}OS_2$ and a small amount of the dihydric alcohol with composition $C_{13}H_{16}O_2S_2$. If the molar ratio of butyllithium to di-2-thienylmethane is 2:1, then on subsequent treatment with ethylene oxide the latter of these two alcohols is obtained in principal amount and the alcohol $C_{11}H_{12}OS_2$ in considerably lesser amount. The total yield (based on di-2-thienylmethane) in both cases is about 90%. Hydrogenation of the alcohol of composition $C_{11}H_{12}OS_2$ with skeletal nickel catalyst gives undecyl alcohol. This establishes the structure of the original alcohol as 5-(β-hydroxyethyl)-di-2-thienylmethane (V). From the properties of its phenylurethane the dihydric alcohol proved to be identical with the condensation product * obtained from 2-(β-hydroxyethyl)-thiophene ** and formaldehyde in the presence of sulfuric acid; from its method of preparation it is 5,5'-bis-(β-hydroxyethyl)-di-2-thienylmethane (VI).

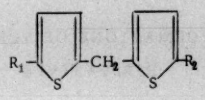
The presented data permit the conclusion that in the reaction of di-2-thienylmethane with n-butyllithium the α-hydrogen atoms are actually replaced by the metal, and that in the action of ethylene oxide on the resulting lithium derivatives the alcohols of structure (V) and (VI) are obtained.

By hydrogenating 5,5'-bis-(β-hydroxyethyl)-di-2-thienylmethane with skeletal nickel catalyst we were able to obtain the glycol of composition $C_{13}H_{28}O_2$ in good yield, which from its melting point is identical with the 1,13-tridecanediol described in the literature [5]. It should be mentioned that the method described here for the synthesis of the indicated glycol through the dithienylmethane is apparently a shorter and more accessible way of obtaining it for preparative purposes. Among other glycols of similar structure the preparation of 1,13-tridecanediol has been accomplished by the general Bouveault method for the reduction of esters [6]; this reaction proceeds with excellent yield; however, the synthesis of the starting brassilic acid is quite complicated.

* The yield of condensation product was very slight.

** See the experimental section for the preparation of 2-(β-hydroxyethyl)-thiophene. This alcohol was synthesized earlier from thienylmagnesium bromide [1] or from thienylmagnesium iodide [13] and ethylene oxide in respective yield of 53 and 65%, and from 2-chlorothiophene [4] by means of sodium amalgam and ethylene oxide (in 47% yield).

With carbon dioxide 5-lithium-di-2-thienylmethane (III) gives di-2-thienylmethane-5-carboxylic acid (VII) in about 70% yield, the hydrogenation of which gives a new acid, comparable to decanoic acid in its properties.



(I) $R_1=R_2=H$,
(II) $R_1=R_2=COCH_3$,
(III) $R_1=H$, $R_2=Li$;
(IV) $R_1=R_2=Li$,
(V) $R_1=H$, $R_2=CH_2-CH_2OH$,
(VI) $R_1=R_2=CH_2-CH_2OH$,
(VII) $R_1=H$, $R_2=COOH$,
(VIII) $R_1=H$, $R_2=COC_4H_9$.

If butyllithium and the dithienylmethane are taken in such proportions that the dilithium derivative is formed, then on subsequent treatment with carbon dioxide a mixture of mono- and dicarboxylic acids is obtained, which mixture we were unable to separate. From the neutral portion of the reaction product we isolated a small amount of oil, which on heating with 2,4-dinitrophenylhydrazine in alcohol gave a crystalline substance, in composition corresponding to the dinitrophenylhydrazone of 5-valeryl-di-2-thienylmethane (VIII). In this connection it is necessary to mention that Gilman and Esmay [7] isolated n-butyl 4-benzothienyl ketone as a by-product in the carbonation of 4-dibenzothienyllithium, obtained by the action of n-butyllithium.

EXPERIMENTAL

All of the experiments with butyllithium were carried out in a nitrogen atmosphere.

Preparation of 5-(β-Hydroxyethyl)-di-2-thienylmethane and 5,5'-Bis-(β-hydroxyethyl)-di-2-thienylmethane.

a) Experiment with 1 Equivalent of Butyllithium. To a solution of 5.4 g (0.03 mole) of the dithienylmethane in 20 ml of dry ether at −5 to 0° was added a solution of 0.03 mole of butyllithium in ether, and the mixture was stirred for 20 minutes. Then a solution of 0.05 mole of ethylene oxide in dry ether was introduced into the mixture at such a rate that the temperature remained below 0°. A large amount of precipitate was obtained. The mixture was decomposed with alcohol and acidulated water, the ether layer was separated, washed, and dried over sodium sulfate. After evaporation of the ether, the residue was vacuum-distilled at 3 mm; 1st fraction 125-150°, 1.3 g of dithienylmethane; 2nd fraction 188-190°, 3.75 g (73.6%); 3rd fraction 220-230°, 0.8 g (13.1%)—on cooling the substance crystallized; after recrystallization from ether, m.p. 50-51°.

Analysis of the 2nd fraction:

Found %: C 58.73, 58.95; H 5.48, 5.64. $C_{11}H_{12}O_2S_2$. Calculated %: C 58.89; H 5.39.

From its composition the 2nd fraction is 5-(β-hydroxyethyl)-di-2-thienylmethane.

Analysis of the 3rd fraction:

Found %: C 58.57, 58.43; H 6.03, 6.06; S 23.68, 23.53. $C_{13}H_{16}O_2S_2$. Calculated %: C 58.15; H 6.01; S 23.88.

From its composition the 3rd fraction is 5,5'-bis-(β-hydroxyethyl)-di-2-thienylmethane.

From 5-(β-hydroxyethyl)-dithienylmethane the phenylurethane with m.p. 73.5-74° (from alcohol) was obtained.

Found %: C 63.06, 63.08; H 5.03, 4.98; S 18.43, 18.51. $C_{18}H_{17}O_2NS_2$. Calculated %: C 62.95; H 4.98; S 18.67.

From 5,5'-bis-(β-hydroxyethyl)-dithienylmethane the phenylurethane with m.p. 140.5-141° (from alcohol) was obtained.

Found %: N 5.55, 5.78. $C_{27}H_{26}O_4N_2S_2$. Calculated %: N 5.53.

b) Experiment with 2 Equivalents of Butyllithium. The reaction of 9 g (0.05 mole) of the dithienylmethane with 0.11 mole of butyllithium and 0.15 mole of ethylene oxide in ether, as indicated above, gave a reaction mixture that was vacuum-distilled at 2 mm: 1) 180-185°, 1.4 g (12.5%) of 5-(β-hydroxyethyl)-di-2-thienylmethane; 2) 221-231°, 10.3 g (77%) of 5,5'-bis-(β-hydroxyethyl)-di-2-thienylmethane.

Hydrogenolysis of 5-(β-Hydroxyethyl)-di-2-thienylmethane. A mixture of 4.4 g of 5-(β-hydroxyethyl)di-2-thienylmethane, 150 ml of ethyl alcohol and about 36 g of skeletal nickel catalyst, prepared by the Billica and Adkins method [8], was boiled for 3 hours with good stirring. The next day the catalyst was filtered and extracted in

the Soxhlet apparatus with alcohol for 8 hours. The alcohol was removed from the reaction product by distillation through a dephlegmator, while the residue was vacuum-distilled. There was obtained 2.55 g (76%) of substance with b.p. 118-120° at 6 mm and n_D^{23} 1.4403.

Found %: C 76.71, 76.53; H 14.03, 14.00. $C_{11}H_{24}O$. Calculated %: C 76.67; H 14.04.

From the alcohol obtained in this manner the phenylurethane with m.p. 61-62° (from alcohol) was prepared. The mixed melting point of this urethane with the phenylurethane of undecyl alcohol, prepared by the hydrogenolysis of 5-(5'-methyl-2-thenyl)-thiophene-2-carboxaldehyde, failed to be depressed.

Literature for undecyl alcohol: b.p. 120° at 7 mm [9], n_D^{23} 1.4392 [10], phenylurethane m.p. 62° [11].

Hydrogenolysis of 5,5'-Bis-(β-hydroxyethyl)-di-2-thienylmethane. A mixture of 2.2 g of the indicated diol, 100 ml of ethyl alcohol and about 21 g of skeletal nickel catalyst was boiled for 4.5 hours with good stirring; further treatment was the same as in the preceding experiment. After distilling off the alcohol there remained 1.6 g of solid substance, which after recrystallization from ether melted at 76°. Yield of pure product 1.4 g (80%).

Found %: C 72.31, 72.48; H 13.10, 13.02. $C_{13}H_{28}O_2$. Calculated %: C 72.16; H 13.04.

In the literature a m.p. of 76.4-76.6° [5] is indicated for 1,13-tridecanediol.

Preparation and Hydrogenolysis of Di-2-thienylmethane-5-carboxylic Acid. a) Experiment with 1 Equivalent of Butyllithium. To a solution of 2.7 g (0.015 mole) of the dithienylmethane in 20 ml of ether at −5 to 0° was added a solution of 0.018 mole of butyllithium in ether. After stirring for 10 minutes the solution was poured into a mixture of dry ice and ether. The resulting lithium salt precipitate was dissolved in water, the water solution was separated from the ether layer, and then acidified with dilute hydrochloric acid. The floating oil was extracted with ether; after removal of the ether there remained 2.4 g (71%) of bright orange solid acid, which after recrystallization from water and 50% alcohol melted at 104-105°. Yield of recrystallized product 2.1 g.

Found %: C 53.57, 53.31; H 3.71, 3.45; S 28.46, 28.31. $C_{10}H_8O_2S_2$. Calculated %: C 53.54; H 3.59; S 28.58.

b) Hydrogenolysis. A mixture of 3.1 g of di-2-thienylmethane-5-carboxylic acid, 3.4 g of soda, 400 ml of water and about 50 g of skeletal nickel catalyst was heated with stirring for 1 hour at 80-90°. The catalyst was filtered and repeatedly washed with dilute soda solution. Acidification of the soda solution with hydrochloric acid gave a white solid, which was extracted with ether. After evaporation of the ether, the residue was vacuum-distilled twice: b.p. 146-148° at 10 mm, yield 1.5 g (63%). The substance crystallized immediately in the receiver.

Found %: C 69.45, 69.64; H 11.58, 11.51. $C_{10}H_{20}O_2$. Calculated %: C 69.72; H 11.70.

For decanoic acid the following constants are given in the literature: m.p. 31.5°, b.p. 148-151° at 11 mm [12].

c) Experiment with 2 Equivalents of Butyllithium. The reaction of 2.7 g (0.015 mole) of the dithienylmethane with 0.03 mole of butyllithium and carbon dioxide, as described above, gave, instead of the expected dicarboxylic acid, 1.5 g of crude product, which after three recrystallizations from water, 50% alcohol and 50% acetic acid had a wide melting range at around 200° (with decompn.).

Found %: C 51.92, 51.83; H 3.52, 3.44; S 24.79, 25.11. $C_{11}H_8O_4S_2$. Calculated %: C 49.23; H 3.01; S 23.90. $C_{10}H_8O_2S_2$. Calculated %: C 53.54; H 3.59; S 28.58.

Judging from the analysis, this substance is a mixture of mono- and dicarboxylic acids. From the ether layer 1 g of oil was isolated, which distilled at 185-195° (5 mm). When heated with an alcohol solution of 2,4-dinitrophenylhydrazine a crystalline substance with m.p. 112° (from alc.) was obtained. From its composition the substance is 5-valeryl-di-2-thienylmethane.

Found %: C 53.74, 53.71; H 4.67, 4.71; N 12.50, 12.36. $C_{20}H_{20}O_4N_4S_2$. Calculated %: C 54.04; H 4.54; N 12.60.

Preparation of 2-(β-Hydroxyethyl)-thiophene. 2-(β-Hydroxyethyl)-thiophene with b.p. 98-102° at 7 mm was obtained, under the conditions described for the dithienylmethane, from 8 g of thiophene with the molar amount of butyllithium and ethylene oxide. Yield 9.5 g (78%), n_D^{20} 1.5445.

Found %: C 62.81, 63.06; H 5.04, 5.13; S 12.48, 12.56. C_6H_8OS. Calculated %: C 63.13; H 5.30, S 12.96.

The phenylurethane was prepared from the alcohol, which after recrystallization from alcohol and petroleum ether melted at 60.5°. The mixed melting point of this urethane with the urethane of 2-(β-hydroxyethyl)-thiophene,

obtained by the method of Blicke and Burckhalter [1], failed to be depressed.

Literature for 2-(β-hydroxyethyl)-thiophene: b.p. 107-109° at 14 mm, phenylurethane, m.p. 57-58° (from petroleum ether) [1]; b.p. 99-100° at 7 mm, n_D^{20} 1.5478, m.p. 52-53° [4].

In addition, 1.2 g of yellow oil was isolated, which distilled at 140-160° (3 mm); apparently, 2,5-bis-(β-hydroxyethyl)-thiophene. Its phenylurethane was prepared; after recrystallization from alcohol, m.p. 154.5-155°

Found %: C 64.53, 64.45; H 5.36, 5.46; S 7.69, 8.02. $C_{32}H_{32}O_4N_2S$. Calculated %: C 64.37; H 5.42, S 7.81.

Preparation of 5,5'-Bis-(β-hydroxyethyl)-di-2-thienylmethane from 2-(β-Hydroxyethyl)-thiophene. 2-(β-Hydroxyethyl)-thiophene (5.2 g), obtained in the preceding experiment, was added at −30 to a solution of 55 g of concentrated sulfuric acid in 65 ml of water, after which 3 ml of 35% formalin was added and the mixture shaken at room temperature for 5 hours. A tarry substance separated on the sides of the vessel; it was washed with water and treated twice with alcohol. The alcohol solution was evaporated in vacuo; from the residue there distilled at about 235° and 4 mm a small amount of pale yellow viscous oil. The oil partially crystallized on cooling; the phenylurethane was prepared from it, which after recrystallization from alcohol melted at 140.5°.

Found %: C 64.12, 63.98; H 5.22, 4.93; S 12.42, 12.16. $C_{27}H_{26}O_4N_2S_2$. Calculated %: C 64.01; H 5.17; S 12.66.

The mixed melting point with the phenylurethane of 5,5'-bis-(β-hydroxyethyl)-di-2-thienylmethane, obtained from the dithienylmethane, failed to be depressed.

SUMMARY

1. The reaction of butyllithium with di-2-thienylmethane gave the mono- and dilithium derivatives, which when reacted with ethylene oxide correspondingly gave 5-(β-hydroxyethyl)-di-2-thienylmethane and 5,5'-bis-(β-hydroxyethyl)-di-2-thienylmethane.

2. The reaction of carbon dioxide with 5-lithium-di-2-thienylmethane gave di-2-thienylmethane-5-carboxylic acid.

3. Hydrogenolysis of the above indicated compounds with skeletal nickel catalyst correspondingly gave undecyl alcohol, 1,13-tridecanediol and decanoic acid.

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MIXED POLYHALO DERIVATIVES OF ACENAPHTHENE. III.

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Earlier we had studied the polychloro and polybromo derivatives of acenaphthene and had established their structure [1]. It was of interest to follow the order of entrance of halogen atoms into the acenaphthene nucleus, and with this in mind we synthesized a number of mixed halogen derivatives of acenaphthene. We started from 5-chloroacenaphthene, which was brominated; as a result the penta- and hexachlorobromo derivatives were isolated. As was described earlier in the preparation of the polychloro and polybromo derivatives, the above were subjected to direct oxidation and to alkaline hydrolysis; here a complete parallelism in the properties of the newly obtained chlorobromo products with the earlier described polyhalides was observed.

The bromination of 5-chloroacenaphthene (I) with sufficient bromine results in the immediate formation of 1,2,3,4-tetrahydro-1,2,3,4,9 (or 10)-pentabromo-5-chloroacenaphthene (V). Consequently, the bromine atoms enter the ring that is devoid of chlorine; here the reaction is one of bromine addition, and not bromine substitution. This is also observed in the bromination of 5-bromoacenaphthene and in the chlorination of 5-chloroacenaphthene.

It can be stated that when a halogen atom enters one of the naphthalene rings, then the second ring becomes clearly unsaturated. The first ring is inactivated; not once were we able to show in the polyhalogenation products the presence of compounds in which there was more than one halogen atom in the unreduced portion of the naphthalene ring.

After the bromine has added, apparently the next step is the bromination of the 5-membered ring with the formation of the hexahalide (V). Already during formation the latter is partially transformed into the pentahalide (III). This transformation can also be accomplished by short heating of the hexahalide in glacial acetic acid.

The direct oxidation of the hexa- and pentahalides (V), (III) results in total cleavage of the bromine and both compounds give the same 4-chloronaphthalic acid (II).

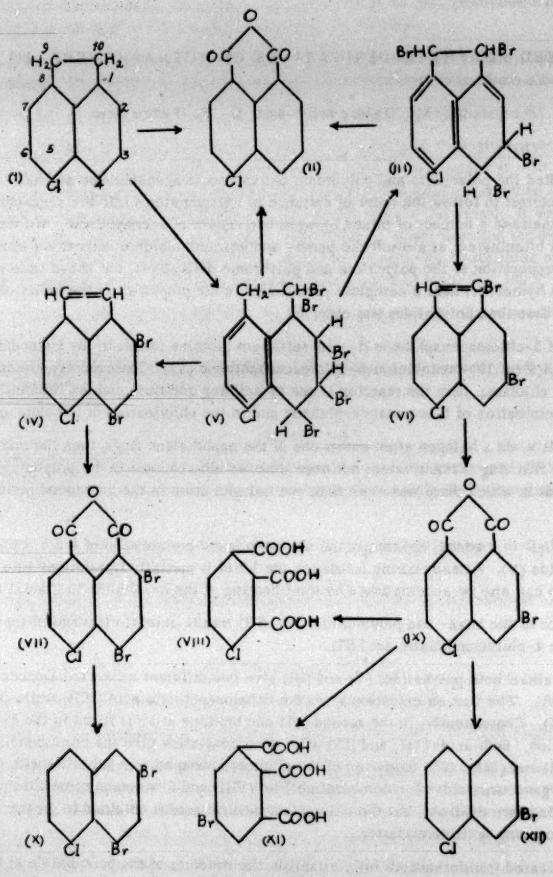
When treated with alkali both polyhalides (V) and (III) give two different mixed trihaloacenaphthylenes: yellow (IV) and orange (VI). The first on oxidation gives the trihalonaphthalic acid (VII), while the second gives the dihalonaphthalic acid (IX). Consequently, in the second (VI) one bromine atom is found in the 5-membered ring, and is removed on oxidation. Both acids (VII) and (IX) after decarboxylation give the corresponding di- and trihalonaphthlene derivatives (X) and (XII). The oxidation of the chlorobromonaphthalic acid (IX) with potassium permanganate in alkaline medium gave two acids—4-chlorohemimellitic (VIII) and 5-bromohemimellitic (XI). Consequently, both of the naphthalene rings are oxidized, but the chlorohemimellitic acid is obtained in greater yield (about 60%), i.e. the bromine-containing ring is oxidized faster.

As a result, the indicated transformations fully establish the structure of the pentahalide as being 3,4-dihydro-3,4,9.10-tetrabromo-5-chloroacenaphthene (III). The structure of the hexahalide (V) follows in part from the above indicated transformations and in part from the analogy with the earlier described hexachloro and hexabromo derivatives [1].

EXPERIMENTAL

Polybromination of 5-Chloroacenaphthene. To a stirred solution of 100 g of 5-chloroacenaphthene in 125 ml of chloroform was added dropwise over 30 minutes a solution of 70 ml of bromine in 50 ml of chloroform. A crystalline precipitate began to deposit even before all of the bromine had been added. The reaction mixture stood until the next day. The obtained crystals were separated and washed several times with small portions of light benzine. The yield of almost colorless crystals was 107.9 g, being a mixture of hexa- and pentahalides (V) and (III).

Separation of the Polyhalides. The polyhalides (107.9 g) were dissolved in 770 ml of hot toluene and let stand for 2 days. The amount of crystallized hexahalide (V) was 71.5 g, while the pentahalide (III) remained dissolved. The solution (mother liquor from the hexahalo derivative) was evaporated to 100 g and allowed to crystallize for 2 days.



The obtained pentahalide (III) crystals were separated, washed with toluene, and air-dried. Yield 25.4 g.

1,2,3,4-Tetrahydro-1,2,3,4,9(or 10)-pentabromo-5-chloroacenaphthene (V). Recrystallization of the obtained 71.5 g of hexahalide (V) from 300 ml of toluene gave 51.8 g of analytically pure product. Colorless crystals, m.p. 154-156° with decomposition. The product is slightly soluble in alcohol, gasoline and ether. Crystallizes from toluene. Gradually yellows on standing. The crude product has to be dried in the air at room temperature, since on heating it decomposes with the liberation of hydrogen bromide.

Found %: C 24.47, 24.50; H 1.42, 1.38. AgCl + AgBr 0.3898, 0.4068 g (from 0.2123, 0.2218 g substance). $C_{11}H_6ClBr_5$. Calculated %: C 24.54; H 1.37. AgCl + AgBr 0.3913, 0.4184 g.*

Oxidation of the Hexahalide (V). A stirred mixture of 4 g of the hexahalide, 15 g of anhydrous sodium dichromate and 80 ml of glacial acetic acid was boiled under reflux for 2 hours.

* The total amount of halide in the mixed halo derivatives was determined and calculated by us as AgCl + AgBr.

Air was passed through the reaction flask from time to time in order to remove the liberated bromine vapors. The reaction product was poured into water and the obtained precipitate was separated and washed free of chromium. The 4-chloronaphthalic acid (II) was extracted from the precipitate by heating with 2% soda solution. The soda solution was acidified, and the precipitated acid was separated and dried. The yield of crude 4-chloronaphthalic anhydride was 0.85 g, which, apparently, contains some bromine.

Found g: AgCl 0.1045, 0.1243 (from 0.1528, 0.1808 g substance). $C_{12}H_5O_3Cl$. Calculated g: AgCl 0.0942, 0.1115.

In the oxidation of the hexahalide (V), the same as for the pentahalide (III), there apparently proceeds partial bromination of the 4-chloronaphthalic anhydride, which can explain the high amount of silver halide obtained.

Two recrystallizations of the crude product from alcohol gave 4-chloronaphthalic anhydride with m.p. 210-211°. The mixed melting point with authentic pure 4-chloronaphthalic anhydride failed to be depressed.

Saponification of the Hexahalide (V). 2,4-Dibromo-5-chloroacenophthylene (IV). To a suspension of 20 g of well-ground hexahalide (V) in 100 ml of benzene was added a solution of 12 g of potassium hydroxide in 100 ml of alcohol. Stirring was continued at room temperature for 1 hour; 200 ml of water was added, the alkali neutralized with acetic acid (to phenolphthalein), impurities removed by filtration, and the benzene removed by distillation from a calcium chloride bath. The resulting precipitate was filtered and dried. Yield 11.5 g, after recrystallization from benzene the yield was 7 g of fine yellow crystals with m.p. 145°.

Found %: C 41.64, 41.62; H 1.50, 1.41. AgCl + AgBr 0.2797, 0.3013 g (from 0.1899, 0.2022 g substance). $C_{12}H_5ClBr_2$. Calculated %: C 41.84; H 1.46. AgCl + AgBr 0.2862, 0.3047 g.

Oxidation of 2,4-Dibromo-5-chloroacenaphthylene (IV). 2,4-Dibromo-5-chloronaphthalic Anhydride (VII). A mixture of 2 g of the trihaloacenaphthylene (IV), 6 g of anhydrous sodium dichromate and 40 ml of glacial acetic acid was boiled under reflux for 30 minutes. The reaction product was diluted with water and the precipitate was filtered and washed free of chromate. The acid was extracted from the precipitate by heating with soda solution. Yield of 2,4-dibromo-5-chloronaphthalic anhydride 1.55 g; colorless crystals, m.p. 208-208.5°.

Found %: C 36.71, 36.78; H 0.80, 0.83. AgCl + AgBr 0.2236, 0.1739 g (from 0.1680, 0.1292 g substance). $C_{12}H_3O_3ClBr_2$. Calculated %: C 36.91; H 0.77. AgCl + AgBr 0.2233, 0.1717 g.

2,4-Dibromo-5-chloronaphthalene (X). A mixture of 2.5 g of the trihalonaphthalic anhydride (VII), 5 g of freshly precipitated mercuric oxide and 40 ml of water was heated in an autoclave for 3 hours at 220°. Then the autoclave was cooled, the CO_2 released, and heating resumed for another 3 hours at 230°. The reaction product was boiled for 1 hour with an equal volume of concentrated hydrochloric acid, cooled, the precipitate separated and then extracted with alcohol. The alcohol solution of the chlorodibromonaphthalene was diluted with water, the precipitate separated and for purification, steam distilled. There was obtained 0.6 g of 2,4-dibromo-5-chloronaphthalene as glistening colorless plates. Silky needles from alcohol, m.p. 139.5-140°.

Found %: C 37.39, 37.33; H 1.62, 1.54. AgCl + AgBr 0.2594, 0.3203 g (from 0.1598, 0.1971 g substance). $C_{10}H_5ClBr_2$. Calculated %: C 37.48; H 1.57. AgCl + AgBr 0.2638, 0.3253 g.

3,4-Dihydro-3,4,9,10-tetrabromo-5-chloroacenaphthene (III). This pentahalide was obtained from the evaporated mother liquor of the hexahalide (V), as described above in the bromination of 5-chloroacenaphthene. It can also be obtained in the following manner. Two grams of the hexahalide (V) is boiled with 50 ml of glacial acetic acid for 45 minutes. After cooling, the obtained crystals are separated, washed with acetic acid, and dried. Yield of pentahalide 0.8 g. Recrystallized from benzene. Colorless needles, m.p. 155° with decomposition.

Found %: C 28.22, 28.29; H 1.42, 1.45. AgCl + AgBr 0.3596, 0.3904 g (from 0.2030, 0.2200 g substance). $C_{12}H_7ClBr_4$. Calculated %: C 28.46; H 1.37. AgCl + AgBr 0.3585, 0.3885 g.

Oxidation of the Pentahalide (III). Run in the same manner as described above for the hexahalide to give the same 4-chloronaphthalic anhydride (II). Consequently, here, also, both bromine atoms are removed from the reduced ring during oxidation.

3,9(or 10)-Dibromo-5-chloroacenaphthylene (VI). To a boiling solution of 25.4 g of the pentahalide (III) in 250 ml of benzene was added a hot solution of 18 g of potassium hydroxide in 250 ml of alcohol and the mixture boiled 15 minutes. The reaction product was diluted with water and then treated the same as described above for the saponification of the hexahalide. Yield of product 16.55 g. Recrystallization from benzene gave 10.3 g of reddish-orange needles with m.p. 167-168°.

Found %: C 41.78, 41.67; H 1.45, 1.50. AgCl + AgBr 0.3040, 0.3095 g (from 0.2021, 0.2068 g substance). $C_{12}H_5ClBr_2$. Calculated %: C 41.84; H 1.46. AgCl + AgBr 0.3045, 0.3116 g.

3-Bromo-5-chloronaphthalic Anhydride (IX). A mixture of 4 g of the trihalide (VI), 20 g of anhydrous sodium dichromate and 80 ml of glacial acetic acid was boiled under reflux for 2 hours. The reaction product was isolated the same as (VIII). Yield of anhydride 3.2 g; colorless crystals, m.p. 205°.

Found %: C 46.18, 46.06; H 1.20, 1.36. AgCl + AgBr 0.1584, 0.1624 g (from 0.1505, 0.1556 g substance). $C_{12}H_4O_3ClBr$. Calculated %: C 46.26; H 1.29. AgCl + AgBr 0.1600, 0.1654 g.

1-Chloro-7-bromonaphthalene (XII). The chlorobromonaphthalic anhydride (IX) (2.5 g) was decarboxylated in the same manner as described above for the trihalonaphthalic anhydride (VII). There was obtained 1.2 g of 1-chloro-7-bromonaphthalene as colorless needles (from alcohol) with m.p. 68-68.5°.

Found %: C 49.59, 49.53; H 2.45, 2.47. AgCl + AgBr 0.2038, 0.2195 g (from 0.1507, 0.1612 g substance). $C_{10}H_6ClBr$. Calculated %: C 49.72; H 2.50. AgCl + AgBr 0.2066, 0.2210 g.

Oxidation of 3-Bromo-5-chloronaphthalic Anhydride (IX). To a solution of 2.3 g of the anhydride (IX) in 100 ml of 0.6% sodium hydroxide solution, heated on the water bath, was added in portions over several minutes a hot solution of 7.4 g of potassium permanganate in 75 ml of water. Heating on the water bath was continued for 3 hours, the residual permanganate destroyed with several milliliters of alcohol and the hot solution filtered from the manganese dioxide. To the filtrate together with wash waters was added 1.8 ml of concentrated sulfuric acid (d 1.84). Again the solution was heated on the water bath and the oxidation completed with a hot solution of 0.75 g of potassium permanganate in 20 ml of water. Heating was continued another 15 minutes, the mixture filtered, and the filtrate evaporated on the water bath to 34 g of residue. From the evaporated solution on cooling there crystallized 0.65 g of the slightly water soluble monopotassium salt of 5-bromohemimellitic acid. The readily soluble potassium salt of 4-chlorohemimellitic acid remains in the filtrate. The acid is isolated from solution in the following manner: the solution is strongly acidified with hydrochloric acid and evaporated to dryness, and from the dry residue 0.8 g of 4-chlorohemimellitic acid is extracted with ether. Both of the obtained hemimellitic acids were characterized by their melting points and elementary analysis. Together with the dihalo derivatives of hemimellitic acids, they were described in detail by us in a previous paper.

SUMMARY

1. A number of mixed polyhalo derivatives of acenaphthene were synthesized and their structure was established.

2. 1-Choro-7-bromonaphthalene and 1-chloro-6,8-dibromonaphthalene were synthesized.

3. It was established that in the bromination of monochloroacenaphthene the bromine adds to the unhalogenated ring.

4. In the oxidation of 3-bromo-5-chloronaphthalic anhydride both the bromine-containing ring and the chlorine-containing are oxidized, but the chlorine-containing ring is oxidized at a slower rate.

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A NEW SYNTHESIS METHOD OF C^{14} LABELED p-AMINOBENZOIC ACID AND PREPARATION OF THE C^{14} LABELED ANESTHETICS ANESTHESINE, NOVOCAINE AND COCAINE

Yu. V. Markova, L. N. Zenkova and M. N. Shchkina

We describe here the preparation of p-aminobenzoic acid, anesthesine (benzocaine) and novocaine (procaine), labeled with C^{14} in the carbonyl group, and of cocaine hydrochloride, labeled in the CO group of the benzoyl radical.

The preparation of p-aminobenzoic acid, labeled in the carbonyl group, is described in the literature [1]. This synthesis was accomplished by the action of n-butyllithium on p-bromoaniline in ether with subsequent carbonation of the resulting p-lithium-N-lithiumbenzene at −80° in an evacuated system. By subsequent decomposition of the carbonation product with dilute hydrochloric acid the above authors obtained p-aminobenzoic acid in 32.8% yield (based on starting $Ba\overset{*}{C}O_3$).

We developed a new method for preparing p-aminobenzoic acid, proceeding from barium carbonate through p-chlorobenzoic acid and ammonolysis of the latter. We obtained p-chlorobenzoic acid by the Gilman method [2], modified and adapted by us for microsynthesis, in 75% yield (based on $Ba\overset{*}{C}O_3$) by reacting n-butyllithium (0.011 mole) with p-bromochlorobenzene (0.011 mole) in ether in a nitrogen atmosphere, followed by carbonation with labeled carbon dioxide gas (0.01 mole) in vacuo at −70°. Gilman ran this reaction with a 50% excess of n-butyllithium and a large excess of solid carbon dioxide under ordinary conditions (at room temperature, without vacuum), where he obtained p-chlorobenzoic acid in 90% yield, based on starting p-bromochlorobenzene. The p-chlorobenzoic acid obtained by us was heated in a closed steel cylinder (bomb) for 4 hours at 140° with a 28% aqueous ammonia solution in the presence of cuprous chloride. After suitable treatment, the labeled p-aminobenzoic acid was obtained in 55.2% of the theoretical yield (based on $Ba\overset{*}{C}O_3$). The p-aminobenzoic acid was converted into anesthesine by esterification with anhydrous ethyl alcohol in the presence of hydrogen chloride [3]. The yield of anesthesine was 55.1% (based on $Ba\overset{*}{C}O_3$).

The re-esterification [4] of anesthesine with diethylaminoethanol in the presence of traces of sodium diethylaminoethanol gave labeled novocaine in 23.4 % yield (based on starting $Ba\overset{*}{C}O_3$).

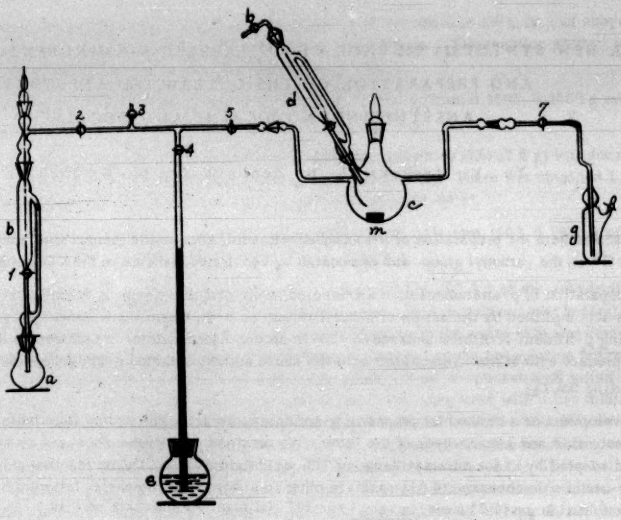
The labeled cocaine was prepared through the C^{14} labeled carboxyl group [5] in benzoic acid, which, with thionyl chloride, was converted into benzoyl chloride [6]. The latter, after good removal of excess thionyl chloride by distillation, without further purification was used for the benzoylation [7] of ecgonine methyl ester. The yield of cocaine hydrochloride was 76% of the theoretical, based on benzoic acid.

The melting points of the substances given in the Experimental Section were determined on model labeled specimens.

EXPERIMENTAL

p-Chlorobenzoic Acid. The p-chlorobenzoic acid was prepared in a special apparatus, consisting of reaction vessel c, fitted with magnetic stirrer m and dropping funnel d, carbonator a, b, manometer e and gooseneck g.

In carbonator a was placed 1.97 g of active barium carbonate. In dropping funnel b was placed 10 ml of concentrated sulfuric acid. In gooseneck g, closed with a soda lime tube, was placed 8 ml of 1 N sodium hydroxide. After this the air was evacuated from the system through stopcock 3 by means of a vacuum pump (with stopcocks 1, 6 and 7 closed), then stopcock 3 was closed and through the same stopcock the apparatus was filled with dry, pure nitrogen. As soon as the apparatus was filled with nitrogen, stopcock 7 was opened and nitrogen was blown through gooseneck g. After dry nitrogen had been blown through the whole system, stopcock 7 was closed, then stopcock 3, and the whole cycle of first evacuating the system and then filling it with nitrogen was repeated, opening stopcock b after the system had been filled with nitrogen.



To a solution of 1.8 g of n-butyllithium in 40 ml of anhydrous ether (the ether solution concentration was determined by titration for total and residual alkalinity [8]), placed in reaction flask c, with constant nitrogen passage and magnetic stirrer mixing at 8-10° (bath temperature), was added from dropping funnel d a solution of 2.3 g of p-bromochlorobenzene in 10 ml of dry ether. After adding the latter, the reaction solution was stirred for another 15-20 minutes at 15° (bath temperature), then the reaction vessel was placed in an acetone-dry ice bath, the system was evacuated and the carbonation run at −70°, adding slowly at first, and then rapidly, sulfuric acid from funnel b to the barium carbonate. To complete the decomposition of the barium carbonate, flask a was heated with a free flame for 3-5 minutes. The whole carbonation process was run for 15-20 minutes at −70° and constant stirring. On conclusion of carbonation the carbon dioxide traces were displaced from the whole apparatus by nitrogen into gooseneck g, where they were absorbed by the sodium hydroxide solution. After blowing nitrogen through the apparatus (7-10 minutes) stopcock 7 was closed, the nitrogen disconnected, and with ice water cooling the reaction solution was acidified with 20 ml of 10% hydrochloric acid. The ether layer was separated, washed 3 times with 10 ml portions of 2 N sodium hydroxide solution, and then with water. The p-chlorobenzoic acid was isolated by acidification of the alkaline solution with concentrated hydrochloric acid. The precipitated acid was filtered, washed with water and dried in a vacuum-desiccator. The yield of p-chlorobenzoic acid was 1.17 g (75% of the theoretical, based on $BaCO_3$), m.p. 238°. There was recovered 5-6% of CO_2 as Na_2CO_3 (in gooseneck g). The carbon dioxide can also be recovered by the method of liquid nitrogen freezing, which gives better results.

p-Aminobenzoic Acid.* A mixture of 1.2 g of p-chlorobenzoic acid, 1.45 g of cuprous chloride (freshly prepared catalyst) and 5 ml of aqueous 28% ammonia solution was heated in a 10-15 ml stainless steel cylinder (bomb) on the oil bath at 138-140° for 4 hours. The reaction solution after cooling was transferred to a separatory funnel, the cylinder was washed several times with water (5 ml portions) and the wash waters were added to the reaction solution. The latter was acidified with hydrochloric acid, extracted twice with ether (10 ml portions), the ether layer separated, and the water solution saturated with hydrogen sulfide. The resulting CuS precipitate was separated, washed with water, and the filtrate evaporated in vacuo to a volume of 16-18 ml. To the residue with cooling was added aqueous ammonia solution until alkaline to litmus, and then 80% acetic acid, until a brown stain with Congo was obtained. The obtained crystals were filtered, washed with 1-2 ml of cold water, and then dried in a vacuum-desiccator. The yield of p-aminobenzoic acid was 0.44 g. Evaporation of the mother liquor in vacuo, washing the dry residue with ether (9 or 10 times), and subsequent removal of the ether by distillation, gave another 0.3 g of

* The ammonolysis of p-chlorobenzoic acid was studied with the assistance of A. A. Karapetyan.

p-aminobenzoic acid. In addition we found that the total yield of p-aminobenzoic acid turned out to be 0.74 g (70.4% of the theoretical, based on ClC_6H_4COOH). Recrystallization from 1.5-2 ml of water with activated charcoal gave 0.65 g of pure p-aminobenzoic acid with m.p. 185°. The mixed melting point with p-aminobenzoic acid, obtained by a different method, failed to be depressed. To prepare anesthesine it is unnecessary to isolate the free p-aminobenzoic acid. After acidifying the aqueous solution of the ammonolysis product with hydrochloric acid, followed by hydrogen sulfide saturation, the resulting CuS precipitate was filtered, washed with water, and the filtrate evaporated in vacuo to dryness. For complete removal of water there was added 10 ml of benzene to the residue, and then distilled. The dry residue, containing the hydrochloride of p-aminobenzoic acid and inorganic salts, was used directly for the following reaction

Anesthesine. To the dry residue, containing the hydrochloride of p-aminobenzoic acid and inorganic salts (see preceding experiment), was added 30 ml of a 4-5% hydrogen chloride solution in anhydrous ethyl alcohol and the mixture boiled under reflux for 4 hours. On conclusion of reaction the alcohol was vacuum-distilled, to the residue was added 40 ml of water, some activated charcoal and hydrosulfite; the solution was boiled for 5 minutes, and filtered. To the filtrate with cooling was added aqueous 10% sodium carbonate solution, the precipitate obtained here was filtered, washed with water, and dried in a desiccator. The yield of anesthesine was 0.93 g (73.5% of the theoretical, based on p-chlorobenzoic acid), m.p. 90-91°. Without further purification the thus obtained anesthesine was used to synthesize novocaine. To obtain pure (pharmacopoeia grade) anesthesine, the latter is recrystallized from 3 ml of 50% ethyl alcohol. Yield 0.8 g.

Novocaine. To 1 g of anesthesine in 2 g of diethylaminoethanol (previously dried and distilled, b.p. 158-160°) was added a solution of 1 mg of metallic sodium in 0.9 g of diethylaminoethanol. From the obtained solution a mixture of diethylaminoethanol and formed ethyl alcohol was rapidly removed by distillation at 76-80° and 35 mm. After distilling off about 1.2 g of this mixture the reaction solution was heated at 80° (40-45 mm) for 1 hour, and then the rest of the diethylaminoethanol was distilled off at 80-85° (20-25 mm). To the heated residue was added 5% hydrochloric acid solution until it gave a brown stain with Congo. After complete solution of the precipitate the reaction mass was neutralized with aqueous 20% sodium hydroxide solution to bromocresol purple indicator (to gray stain), then hydrosulfite and activated charcoal were added, and the mixture was let stand until the next day for isolation of unreacted anesthesine. To the filtered solution at 8-10° was added 20% sodium hydroxide solution until it showed alkaline to phenolphthalein. The obtained precipitate was filtered, washed with water, and desiccator-dried. The yield of novocaine base was 1.8-1.9 g. This was recrystallized from 0.9 ml of isopropyl alcohol. After 12 hours standing at 0-2° the resulting precipitate (about 1 g) was separated, water was added to it (5 ml), then 0.3 ml of hydrochloric acid; the mixture heated and at 60° hydrochloric acid added in drops until a gray stain was obtained with bromocresol purple paper. After ether extraction the aqueous solution was made alkaline with 20% sodium hydroxide solution (to phenolphthalein). The resulting precipitate (1-1.1 g) was filtered, washed with water, 0.4 ml of water added to it, the mixture acidified to Congo with concentrated hydrochloric acid (0.3-0.35 ml), and at 50° 1.4 ml of saturated sodium chloride solution added. The obtained precipitate after cooling was separated, washed with saturated sodium chloride solution (0.4 ml), and dried in a vacuum-desiccator. Recrystallization from anhydrous ethyl alcohol (7 ml) gave 0.6 g of novocaine hydrochloride with m.p. 156°. Evaporation of the mother liquor gave another 0.1 g of novocaine hydrochloride. Total yield 0.7 g (42.5% of the theoretical, based on starting anesthesine).

Cocaine Hydrochloride. A solution of 0.65 g of labeled benzoyl chloride and 1 g of ecgonine methyl ester in 2 ml of anhydrous benzene was heated under reflux on the water bath for 6 hours. The obtained precipitate was filtered, washed twice with anhydrous benzene (1-2 ml portions), then with anhydrous ether, and dried in a vacuum-dessicator. The yield of cocaine hydrochloride was 1.35 g, m.p. 192°. Evaporation of the benzene solutions gave about 0.1 g more of substance. The total yield of cocaine hydrochloride was 1.45 g. To prepare pharmacopoeia grade cocaine hydrochloride the latter was recrystallized from an alcohol-ether mixture (3 ml of ethyl alcohol and 5 ml of ether). There was obtained 1 g of cocaine hydrochloride with m.p. 192°.

SUMMARY

1. A new method for the preparation of C^{14} labeled p-animobenzoic acid was developed.

2. From p-aminobenzoic acid was obtained anesthesine, labeled in the carbonyl group, and from it novocaine, labeled with C^{14} in the carbonyl group.

3. Cocaine hydrochloride was prepared, labeled with C^{14} in the carbonyl group of the benzoyl radical.

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REACTION OF FREE RADICALS IN SOLUTIONS

III. THE REACTIONS OF FREE RADICALS WITH SULFUR

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The ability of sulfur to react in various ways with free radicals follows from a number of investigations devoted to a study of the influence of sulfur on polymerization and oxidation processes. It is known that sulfur inhibits the polymerization of vinyl acetate [1], stuyrene [2], and mixtures of divinyl (butadiene) with styrene [3]. In the polymerization of chloroprene, sulfur enters into the composition of the polymer chain with the formation of polysulfide and disulfide bonds [4, 5]. However, up to now direct experimental data fail to exist in the literature on the study of free radical reactions with sulfur, and our work is the first attempt in this direction.

We studied the reaction of the methyl, ethyl, isopropyl and allyl free radicals with sulfur and some sulfur-containing compounds in isopropylbenzene solution.

EXPERIMENTAL METHOD AND ANALYSES

The alkylphenyltriazenes were used as our source of free radicals, and also azobenzene, both of which, under the proper temperature conditions, are decomposed in hydrocarbon solution with the formation of free radicals:

$$R-N=N-NHC_6H_5 \rightarrow R\cdot + N_2 + \cdot NHC_6H_5,$$

$$C_6H_5CH_2-N=N-CH_2C_6H_5 \rightarrow 2C_6H_5CH_2\cdot + N_2.$$

The mechanism of this reaction with respect to a large group of alkylphenyltriazenes and some azo compounds was studied in detail earlier [6].

The corresponding triazenes ($CH_3N=N-NHC_6H_5$, $C_2H_5N=NNHC_6H_5$, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\!CHN=NNHC_6H_5$, $CH_2=$ $=CH-CH_2-N=N-NHC_6H_5$) were synthesized by the method of phenyl azide coupling with alkylmagnesium halides [7]. All of the indicated compounds are decomposed in hydrocarbon solution at 100-120°. The selection of isopropylbenzene as solvent is conditioned by the fact that as hydrogen donor in the reactions with free radicals, it hardly differs from cyclohexene, which compound typifies the structure of the 1,4-butadiene link in polymeric chains. With active radicals (R·) the reaction for H-atom cleavage from isopropylbenzene proceeds smoothly with the formation of RH. In this way, it became possible to evaluate the concurrently proceeding reactions of free radicals with sulfur and solvent.

A solution of the triazene and sulfur in isopropylbenzene was heated at 112° until gas evolution ceased. The triazene concentration in the solution was 3.8 mole %, while the sulfur was taken in the ratio of 6-8 moles for 1 mole of triazene. The gas evolved in the decomposition of the triazenes was passed through a trap, cooled at −78°, to condense the mono- and disulfides, then washed with 0.05 N $AgNO_3$ solution to remove mercaptans and hydrogen sulfide, and finally collected in a gas burette. On conclusion of reaction, the amount of hydrocarbons (methane, ethane, propane and unsaturates) in the gas was determined. In the traps, the amount of mercaptan, mono- and disulfides was determined. In the reaction mixture, remaining in the ampoule after triazene decomposition, the amount of di- and polysulfides was determined. For this the cooled solution was separated from unreacted sulfur by filtration, after which the disulfide was vacuum-distilled from the solution. The residual product was diluted with solvent and shaken with metallic mercury, which extracted both free and bound polysulfide sulfur. As a result of this reaction the disulfide is formed:

$$RS-S_m-SR + m\ Hg \rightarrow RSSR + m\ HgS.$$

After the mercury treatment, the amount of disulfide was determined by its reduction with zinc dust in acetic acid medium. The resulting mercaptan was distilled and absorbed in standard silver nitrate solution [8].

Reaction of Methyl, Ethyl and Isopropyl Radicals with Sulfur

In preliminary experiments it was established that the decomposition kinetics of triazenes, determined by the rate of gas evolution, is independent of sulfur presence. This situation is illustrated in Fig. 1.

The alkyl radicals, formed in the decomposition of the corresponding triazenes, are capable of cleaving hydrogen from the solvent (LH) with the formation of RH: $R\cdot + LH \rightarrow RH + L\cdot$. When this reaction is run in the presence of sulfur, the formation, together with RH, of mercaptans, mono-, di- and polysulfides can be expected, in accord with the schemes:

$$R\cdot + S \rightarrow RS\cdot;$$
$$RS\cdot + LH \rightarrow RSH + L\cdot;$$
$$RS\cdot + R\cdot(L\cdot) \rightarrow RSR(RSL);$$
$$2RS\cdot \rightarrow RSSR;$$
$$R\cdot + S_8 \rightarrow RS_8\cdot \rightarrow RS_mR.$$

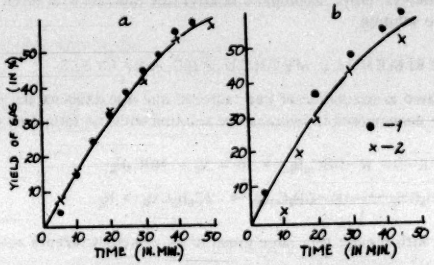


Fig. 1. Decomposition kinetics of triazenes in isopropylbenzene solution at 112°.
1) in the absence of sulfur, 2) in the presence of sulfur. a) methylphenyltriazene, b) allylphenyltriazene.

The yield of RH products in the case of the methyl, ethyl and isopropyl radicals when the reaction is run in isopropylbenzene is respectively 60, 37 and 13% of the theoretical [6]. In Table 1, we give the composition of the decomposition products of alkylphenyltriazenes in the presence of sulfur.

TABLE 1

Composition of the Reaction Products of Free Radicals with Sulfur in Isopropylbenzene Solution at 112°. (Concentration of triazene 3.8 mole %, 6-8 moles of sulfur for 1 mole of triazene)

Radical R	In the Absence of Sulfur	In the Presence of Sulfur				
		Yield (in %)				
	Yield of RH (in %)	RH	RSH	RSR	RSSR	RS_mR
CH_3	60	2.7	0	0	1	62-68
C_2H_5	37	1	0	0	1	38-40
$(CH_3)_2CH$	13	0.9	0	0	0	45-57
$CH_2=CH-CH_2$	0.3	0	0	0	0	13

When methylphenyltriazene is decomposed in isopropylbenzene in the presence of sulfur, the yield of methane is only 2.7%. Neither mercaptan nor monosulfide was found in the reaction products. The yield of dimethyl disulfide

was insignificant (about 1%). The main reaction product of the methyl radical with sulfur is dimethyl polysulfide, formed in 62-68% yield.

We obtained similar results when the reaction of the ethyl and isopropyl radicals with sulfur in isopropylbenzene solution was studied. The amount of ethane and propane in the evolved gas was also insignificant (0.9-1.0%). Neither mercaptans nor monosulfides were found in the reaction products. The main products from the reaction of the ethyl and isopropyl radicals with sulfur, the same as for the methyl radical, are the diethyl and diisopropyl polysulfides. Consequently, the methyl, ethyl and isopropyl radicals, arising in the decomposition of the corresponding triazenes, are almost completely absorbed by sulfur with the formation of polysulfides:

$$R\cdot + (S)_8 \rightarrow RS_8\cdot \rightarrow RS_mR.$$

Of interest is the fact that the indicated radicals differ sharply in their activity as regards H-atom cleavage from isopropylbenzene (based on the yield of RH) and differ but slightly in their reaction with sulfur (based on yield of polysulfides), which situation is associated with the lower energy of activation of the second reaction.

The decomposition of alkylphenyltriazenes in hydrocarbon media results in the formation of considerable aniline and alkylanilines. It is known that many amines under certain conditions will accelerate the addition of sulfur to disulfides with the formation of polysulfides [9]. In this connection there arose the danger that the formation of polysulfides in the decomposition of triazenes in the presence of sulfur is determined to a large degree by secondary reactions, proceeding with aniline and alkylaniline participation.

We studied the reaction of diethyl disulfide with sulfur in the presence of aniline and monomethylaniline at 112° in xylene solution for the purpose of elucidating the influence of these compounds on the process for the formation of diethyl polysulfide.

Diethyl disulfide was synthesized from ethyl iodide and sodium disulfide [10]. The isolated product distilled at 152-154°, $n_D^{19.5}$ 1.5090 (literature [10] b.p. 152.8-153.4°, n_D^{20} 1.5063). A solution of diethyl disulfide in xylene was heated in the presence of sulfur and amines for 5 hours at 112°. The solution concentration of the diethyl disulfide was 8 wt. %, the sulfur was taken in the ratio of 2 moles or more for 1 mole of disulfide. In the reaction products were determined the amount of unreacted diethyl disulfide and the amount of formed polysulfide. For this the diethyl disulfide and solvent were distilled from the reaction mixture at 40-50° and 10 mm. Together with the diethyl disulfide, the diethyl trisulfide also distilled. In one distillate portion after its treatment with mercury, the total amount of diethyl disulfide was determined by zinc reduction in acetic acid medium, with subsequent determination of the mercaptan. In another distillate portion the total amount of polysulfide sulfur was determined by the method of Bolotnikov and Gurova [11].

TABLE 2

Reaction of Diethyl Disulfide with Sulfur in the Presence of Amines at 112°

Amine	Amount of Amine (in Moles for 1 Mole of Disulfide)	Found (in % of Introduced Disulfide)	
		Unreacted disulfide	Diethyl trisulfide
–	–	99.0	0.79
Aniline	1:5	98.8	1.17
Aniline + methylaniline	1:2	97.5	0.63
	1:2		

The obtained data presented in Table 2, show that aniline and methylaniline, under the conditions adopted for the decomposition of triazenes, do not facilitate the formation of polysulfides from the disulfide.

Consequently, the alkyl polysulfides appear as the primary reaction product of free radicals with sulfur.

Reaction of the Allyl Radical with Sulfur

The allyl radical is quite inactive in the reaction for H-atom cleavage from solvents. The total yield of propylene when allylphenyltriazene is decomposed in isopropylbenzene is only 0.3%.

Unsaturates are not found in the liberated gas when allylphenyltriazene is decomposed in the presence of sulfur. Instead, a benzene insoluble tar, containing 20% sulfur, is found in the reaction mixture. The tar is devoid of nitrogen, which indicates that it was formed without the participation of aniline or aniline-containing radicals. In addition, neither mercaptans, diallyl monosulfide or diallyl disulfide were found in the reaction products. For determining diallyl polysulfide, we used the same method as in the other cases, – treatment of the reaction mixture

with mercury to remove both elementary and polysulfide sulfur. However, the diallyl disulfide obtained here differs from the other disulfides in the composition of its zinc reduction products in acid medium. As is known, in the case of the alkyl disulfides there is quantitative formation of mercaptans. In the case of diallyl disulfide, the reduction products are hydrogen sulfide and diallyl monosulfide [12]. The reaction proceeds in accord with the equation:

$$CH_2=CH-CH_2-S-S-CH_2-CH=CH_2 + H_2 \rightarrow H_2S +$$
$$+ CH_2=CH-CH_2-S-CH_2-CH=CH_2.$$

We assumed that the amount of diallyl disulfide in solution could be determined from the amount of evolved hydrogen sulfide. This assumption was verified on the example of pure diallyl disulfide, synthesized by us from allyl bromide and sodium disulfide [13]. As experiment revealed, the yield of hydrogen sulfide in the reduction of diallyl disulfide is close to 100%. On this basis we calculated from the hydrogen sulfide the yield of diallyl polysulfide in the reaction of the allyl radical with sulfur. The determinations revealed that the yield of polysulfide is about 12%.

The low yield of diallyl polysulfide must be attributed to the instability of these products, which was shown by special experiments. The diallyl disulfide was heated in a sealed ampoule at 117° for 10 hours. On conclusion of heating, the reaction mixture was vacuum-distilled (16 mm). The following fractions were isolated (Table 3).

TABLE 3

Thermal Decomposition of Diallyl Disulfide

Fraction Nos.	Temperature	Weight of Fractions (in % of the Original)	Elementary Composition (in %)		
			C	H	S
1	To 76°	20.8	63.18	7.90	28.88
2	76-78	24.8	49.56	6.86	42.09
3	78-90	20.3	49.27	6.48	44.36
4	Residue above 90	25.3	45.63	4.45	49.07

From the elementary analysis data the 1st fraction corresponds to the monosulfide. The composition of the 2nd and 3rd fractions corresponds to diallyl disulfide. In the residue (4th fraction) the sulfur content is considerably above that required for diallyl disulfide.

Thus, diallyl disulfide is an unstable product, easily decomposed at 117° with the formation of the monosulfide.

These data show that in contrast to the more thermostable saturated disulfides, decomposing at the S–S bond on reduction, the disulfides of type $RCH=CH-CH_2-S-S-CH_2-CH=CHR$ are preferentially cleaved at the C–S bond, which is determined by the conjugation of this bond with the C=C bond. This explains the low stability of the disulfide bonds in the main chain of diene polymers.

Apparently, the allyl polysulfides are even less stable products.

From all of the above it follows that in the case of allyl radical formation in polymer chains, – for example, in the dehydrogenation of the α-methylene group with sulfur. – the reaction with sulfur proceeds with the formation of more complex and less stable products than for the reaction with saturated radicals.

Reaction of Azobenzene with Sulfur

As a source of free radicals of the type not formed in the decomposition of aniline and its derivatives, we took azobenzyl, which gives two benzyl radicals:

$$C_6H_5CH_2-N=N-CH_2C_6H_5 \rightarrow 2C_6H_5-CH_2^{\cdot} + N_2.$$

The decomposition of azobenzyl proceeds at higher temperatures than does the decomposition of triazenes. In the absence of sulfur about 60% of the nitrogen is evolved after 14.5 hours at 143°.

The evolution of nitrogen is practically nil when azobenzyl is decomposed in the presence of 13.7 moles of sulfur for 1 mole of azobenzyl. The liberated gas is completely absorbed by a 10% $CdCl_2$ solution with the formation of CdS. The yield of hydrogen sulfide is 81-87%. The reaction products were shown to contain benzalazine in 51% yield. The product had m.p. 93°; its mixed melting point was 93°. Its nitrogen content was 13.75% (calculated: 13.45%).

The formation of hydrogen sulfide and the aldazine is, apparently, due to the oxidation of the azobenzyl by sulfur in accord with the reaction:

$$C_6H_5CH_2N=N-CH_2C_6H_5 + S \rightarrow C_6H_5CH=N-N=CHC_6H_5 + H_2S.$$

The obtained results give basis to assume that similar dehydrogenation reactions are also possible under certain conditions in rubber molecules, containing diallyl groupings, with the formation of a conjugated system of double bonds, for example, in the reaction with sulfur:

$$-CH_2CH=CH-CH_2-CH_2-CH=CH-CH_2-+S\rightarrow$$
$$\rightarrow -CH_2-CH=CH-CH=CH-CH=CH-CH_2-+H_2S.$$

Reaction of the Methyl Radical with Sulfur in the Presence of Mercaptans or Hydrogen Sulfide

Due to the fact that the system during vulcanization can contain mercaptans and hydrogen sulfide, it was necessary to study the reaction of free radicals with sulfur in the presence of these compounds. The reaction was studied on the example of the more active methyl radical in the presence of lauryl and propyl mercaptans or hydrogen sulfide under the same temperature conditions as in the absence of mercaptan. The mercaptans were taken in the ratio of 2 moles of mercaptan for 1 mole of triazene. With propyl mercaptan, the reaction was run in sealed ampoules. The experiments with hydrogen sulfide were run by the method of passing this compound into the reaction mixture during the whole reaction time. The gaseous reaction products were analyzed for the amount of methane. In the reaction mixture was determined the amount of unreacted mercaptan and, by the above described method, the amount of dimethyl disulfide and dimethyl polysulfide.

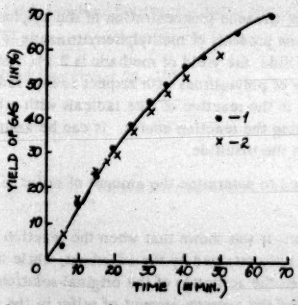


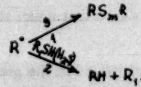
Fig. 2. Kinetics of methylphenyltriazene decomposition in isopropylbenzene solution at 112° in the presence of lauryl mercaptan sulfur.

1) in the presence of sulfur, 2) in the presence of sulfur and mercaptan.

Previously, it was established that mercaptans fail to exert appreciable influence on the kinetics of triazene decomposition (Fig. 2). The experimental data for this are given in Table 4.

From the presented date, it follows that in the joint presence of sulfur and mercaptans (or hydrogen sulfide) the yield of methane in the gas is sharply increased. In the case of lauryl mercaptan, the methane yield is 41.5%. Similar results are obtained when methylphenyltriazene is decomposed in the presence of propyl mercaptan and sulfur (the yield of methane is 39%). When methylphenyltriazene is decomposed in the joint presence of hydrogen sulfide and sulfur the yield of methane is somewhat lower at 30%. The lower methane yield in this case is explained by the lower hydrogen sulfide concentration, the solubility of which in isopropylbenzene at 112° is 0.5 mole %, while the mercaptan content was 3.0 mole %.

As a result, in the presence of mercaptan (or hydrogen sulfide) and sulfur, the main reaction of a free methyl radical is the cleavage of hydrogen from the mercaptan or hydrogen sulfide. Of the two reaction directions (see Scheme below) the second one is predominant.



Reaction of the Methyl Radical with Polysulfides

For a fuller understanding of the reaction directions of free radicals, it was necessary to study their reaction with polysulfides, formed in the initial stage of the process. We studied the reactivity of the methyl group with dilauryl and dibenzyl tetrasulfides.

TABLE 4

Composition of the Reaction Products of the Methyl Radical with Sulfur in the Presence of Mercaptans and Hydrogen Sulfide at 112°

(Concentration of methylphenyltriazene in solution 1.55 mole %)

Composition of the System	Amount of Mercaptan or H_2S in Solution (in mole %)	Yield (in %)			
		CH_4	$CH_3S_mCH_3$	H_2S *	Recovered Mercaptan (in % of Original)
Without sulfur	0	51			
With sulfur	0	2.7	65		
Sulpher + lauryl mercaptan	3.0	41.5	9	14.1	2.7-3.1
Sulfur + propyl mercaptan	3.0	39	–	11	6.3
Sulfur + H_2S	0.5	30	18.4	–	–

* The yield of H_2S that should be obtained in the complete oxidation of the mercaptan was taken as 100%.

The indicated tetrasulfides were synthesized from the corresponding mercaptans and sulfur polychloride [14]. The isolated dilauryl tetrasulfide had the following constants: d_4^{18} 0.9688, S content 27.91% (calculated : 27.44%). After recrystallization the dibenzyl tetrasulfide had m.p. 48-50° (literature: m.p. 49-50°).

The tetrasulfides were taken in the ratio of 3 moles for 1 mole of triazene (concentration of methylphenyltriazene 0.75 mole %). A study of the composition of the decomposition products of methylphenyltriazene in isopropylbenzene at 112° revealed that in the presence of dilauryl tetrasulfide, the yield of methane is 2.1%, while in the presence of dibenzyl tetrasulfide it is 1.3%. The absorption ability of polysulfides with respect to free radicals is similar to the absorption ability of sulfur. From this, it follows that in the reaction of free radicals with sulfur the composition of the formed polysulfides is variable and changes during the reaction course. It can be assumed that the ability to react with free radicals will drop sharply, beginning with the trisulfide.

The chromatographic method using radioactive sulfur S^{35} was used to determine the amount of sulfur in dimethyl polysulfide. **

In previous experiments, performed by S. E. Bresler and coworkers, it was shown that when the reaction mixture was passed through an adsorbent (silica gel) the polysulfides are firmly retained by the adsorbent, while the free sulfur is completely eluted by the solvent. From the difference between the activities of the original solution (reaction mixture) and the solution, freed of polysulfides, was calculated the average amount of sulfur in the polysulfide. The analytical data revealed that on the average the dimethyl polysulfide molecule contains 6 atoms of sulfur.

Chemically, the behavior of polysulfide bonds is similar to that of free sulfur. They are easily cleaved in the development of oxidative and other reactions, accompanying the formation of free radicals.

SUMMARY

1. The main reaction product of free aliphatic radicals with sulfur (under model conditions) are polysulfides. The formed polysulfides react with free radicals in the same manner as elementary sulfur.

On the example of dimethyl polysulfide, it was shown that under the selected process conditions the polysulfide molecule contains on the average 6 atoms of sulfur.

2. The reaction of free radicals with sulfur is suppressed in the presence of mercaptans or hydrogen sulfide. Here the process is predominantly in the direction of rupture of the S–H bond with the formation of the radical RS· (or ·SH).

** S. E. Bresler participated and was consulted in the work on the use of the chromatographic method for separating the reaction products.

3. The reactions of allylphenyltriazene and azobenzyl with sulfur were studied. It was established that the diallyl disulfides are considerably less stable than the corresponding saturated disulfides.

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ABSORPTION SPECTRA OF TETRAALKYLTETRAHYDROFURANDIONES AND SOME OF THEIR DERIVATIVES IN THE ULTRAVIOLET AND VISIBLE REGIONS

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As was shown earlier [1, 2], the crimson-red tetraalkyltetrahydro-3,4-furandiones when dissolved in water or aqueous alcohol lose their color, forming colorless solutions. In the present work, we studied the absorption spectra of these compounds for the purpose of following their spectral changes when dissolved in water, and to elucidate their hydration character.

Our absorption spectra were taken in the visible and ultraviolet regions for isooctane and heptane solutions of 2,2,5,5-tetramethyltetrahydro-3,4-furandione, 2,5-dimethyl-2,5-diethyltetrahydro-3,4-furandione, 2,2,5,5-bis(tetramethylene)-tetrahydro-3,4-furandione, 2,2,5,5-bis(pentamethylene)-tetrahydro-3,4-furandione and 2,2,5,5-tetraphenyltetrahydro-3,4-furandione [3]. All of the investigated diketones possess similar spectra: they have two absorption bands—the first in the visible region (specifically, the compounds in this region are characterized by color) with a well defined wave structure, and the second band in the ultraviolet region, having a vaguely defined wave structure [for the tetraphenyl derivative, the wave structure in the visible absorption band is more weakly defined, and in the ultraviolet region it is completely absent (Fig. 1)]. The first band is characteristic for α-diketones; similar bands with such characteristic absorption band fine structures are observed for glyoxal and diacetyl [4], only in our case, apparently, due to the influence of the cyclic bound oxygen this band is shifted toward the longer wave lengths, which determines the crimson color of the compounds. The spectra of water solutions of 2,2,5,5-tetramethyltetrahydro-3,4-furandione and 2,5-dimethyl-2,5-diethyltetrahydro-3,4-furandione, and also the aqueous-alcohol solutions of 2,2,5,5-bis(tetramethylene)-tetrahydro-3,4-furandione, 2,2,5,5-bis(pentamethylene)-tetrahydro-3,4-furandione and 2,2,5,5-tetraphenyltetrahydro-3,4-furandione • resemble each other and do not have absorption bands in the visible region, while the absorption bands in the ultraviolet fail to have a wave structure (Fig. 2, Table 1).

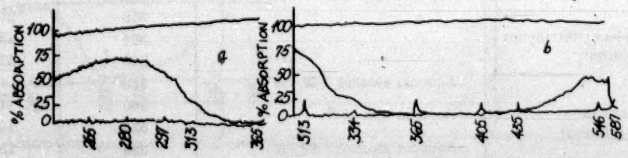


Fig. 1. Absorption spectra of 2,2,5,5-tetramethyltetrahydro-3,4-furandione in isooctane ($c = 1.32 \cdot 10^{-2}$). a) in the ultraviolet region (d = 0.1 cm), b) in the visible region (d = 0.4 cm).

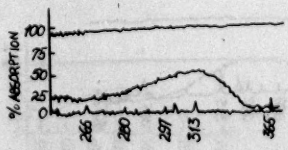


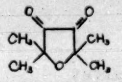
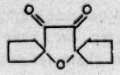
Fig. 2. Absorption spectra of 2,2,5,5-tetramethyltetrahydro-3,4-furandione in water ($c = 2.79 \cdot 10^{-2}$, d = 0.4 cm).

Fig. 3. Absorption spectra of 2,5-dimethyl-2,5-diethyltetrahydro-3-furanone in isooctane ($c = 4.82 \cdot 10^{-2}$, d = 0.4 cm).

• We were unable to take the absorption spectra of the latter substances in water solution due to their poor solubility.

TABLE 1

Absorption Spectra of Diketones

Structural Formula, Name and Constants	Solvent and Mole Concentrations	$\lambda_{max.}$	$\epsilon_{max.}$
		561	19
		536	22
		521	22
	Isooctane $1.32 \cdot 10^{-2}$	333	16
		314	50
2,2,5,5-Tetramethyltetrahydro-		301	110
3,4-furnandione; m.p. 54-56°,		290	170
b.p. 85-85.5° (30 mm).	Water $2.79 \cdot 10^{-2}$	317	29
		566	21
		538	24
2,5-Dimethyl-2,5-diethyltetrahydro-		524	24
3,4-furandione; b.p. 93-95° (16 mm).	Isooctane $7.04 \cdot 10^{-2}$	333	18
n_D^{20} 1.4422, d_4^{20} 1.0062		313	64
		300	140
		289	240
	Water $3.77 \cdot 10^{-2}$	279-290	25
		546	20
		521	23
		510	23
	Heptane $3.4 \cdot 10^{-2}$	332	71
		316	210
2,2,5,5-Bis(tetramethylene)-tetrahydro-		305	320
3,4-furandione; m.p. 37°,		289	400
b.p. 138-140° (14 mm)	Aqueous Alcohol $2.37 \cdot 10^{-2}$	319	38
		570	25
		529	28
		516	28
	Heptane $1.58 \cdot 10^{-2}$	332	94
		318	260
2,2,5,5-Bis(pentamethylene)-tetrahydro-		304	450
3,4-furandione; m.p. 69-70°,		292	525
b. p. 169-170° (16 mm)	Aqueous alcohol $7.62 \cdot 10^{-3}$	323	41
2,2,5,5-Tetraphenyltetrahydro-	Heptane $9.6 \cdot 10^{-3}$	560	140
3,4-furandione; m. p. 109-110°		524	160
	Aqueous alcohol $2.83 \cdot 10^{-3}$	328	256

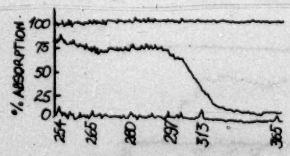


Fig. 4. Absorption spectra of 2,2,5,5-tetramethyl-tetrahydro-3-furanone in water ($c = 3.52 \cdot 10^{-2}$, d = 0.4 cm).

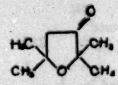
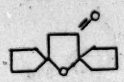
Fig. 5. Absorption spectra of 2,phenyl-4,4,6,6-bis(tetra-methylene)-3,4-furoimidazole in methyi alcohol ($c = 2.48 \cdot 10^{-4}$, d = 0.8 cm).

The changes taking place in the spectra of the water and aqueous-alcohol solutions are undoubtedly associated with hydration. To elucidate the hydration character we took the absorption spectra of the monoketones—2,2,5,5-tetramethyltetrahydro-3-furanone, 2,5-dimethyl-2,5-diethyltetrahydro-3-furanone, 2,2,5,5-bis(tetramethylene)-tetrahydro-3-furanone and 2,2,5,5-bis(pentamethylene)-tetrahydro-3-furanone in isoctane and in water. For all of

the monoketones in isoctane solution there is observed an absorption band in the 300-320 mμ region with a characteristic wave structure (Fig. 3). In water solutions of the same substances the wave structure vanishes, probably due to hydration of the carbonyl group (Fig. 4, Table 2). The spectral similarity of water solutions of the mono- and diketones permits, with sufficient assurance, the assumption that the hydration takes place at the two carbonyl groups.

TABLE 2

Absorption Spectra of Monoketones

Structural Formula, Name and Constants	Solvent and Mole Concentrations	$\lambda_{max.}$	$\epsilon_{max.}$
	Isooctane $4.82 \cdot 10^{-2}$	321	7
		310	12
		301	13
2,2,5,5-Tetramethyltetrahydro-3-furanone; b.p. 149-149.5° (762 mm), n_D^{20} 1.4202, d_4^{20} 0.9249	Water $3.52 \cdot 10^{-2}$	294	42
2,5-Dimethyl-2,5-diethyltetrahydro-3-furanone; b.p. 90-91° (25 mm), n_D^{20} 1.4383, d_4^{20} 0.9319	Isooctane $5.02 \cdot 10^{-2}$	322	10
		310	15
		301	17
	Heptane $6.04 \cdot 10^{-2}$	320	12
		309	20
		299	23
		280	28
		267	28
2,2,5,5-Bis(tetramethylene)-tetrahydro-3-furanone; b.p. 111.5-112° (9 mm), n_D^{20} 1.4855, d_4^{20} 1.0446	Aqueous alcohol $1.43 \cdot 10^{-2}$	295	280
2,2,5,5-Bis(pentamethylene)-tetrahydro-3-furanone; b.p. 141-142° (9 mm), n_D^{20} 1.4941, d_4^{20} 1.0336	Heptane $3.79 \cdot 10^{-2}$	319	12
		308	21
		298	25

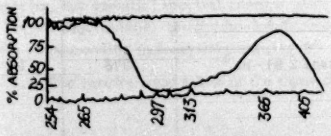


Fig. 6. Absorption spectra of 2,2,4,4-tetramethyltetrahydro-3,4-furo-6,7-dihydropyrazine in isoctane ($c = 1.69 \cdot 10^{-3}$, d = 0.4 cm).

Fig. 7. Absorption spectra of 2,3-dimethyl-2,4-diethyltetramethyl-tetrahydro-3,4-furoquinoxaline in isooctane ($c = 4.94 \cdot 10^{-4}$, d = 0.4 cm).

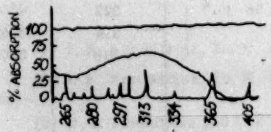


Fig. 8. Absorption spectra of 3-hydroxy-5,5,7,7-bis-(pentamethylene)-tetrahydro-3,4-furo-1,2,4-triazine in methyl alcohol ($c = 3.33 \cdot 10^{-3}$, d = 0.2 cm).

Fig. 9. Absorption spectra of 2,2,5,5-bis(pentamethylene)-tetrahydro-3,4-furandione monosemicarbazone in ethyl alcohol ($c = 1.38 \cdot 10^{-2}$). I – d = 0.1 cm, II – d = 0.4 cm.

TABLE 3

Absorption Spectra of Diketone Derivatives

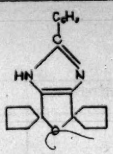
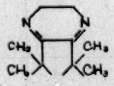
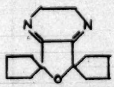
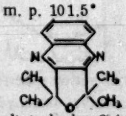
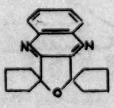
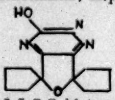
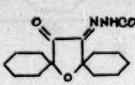
Nos.	Structural Formula, Name and Constants	Solvent and Mole Concentration	$\lambda_{max.}$	$\epsilon_{max.}$
				
1	2-Phenyl-4,4,6,6-bis(tetramethylene)-tetrahydro-3,4-furoimidazole; m.p. 204.5-205.5°	Methyl alcohol $2.48 \cdot 10^{-4}$	295	1600
2	2-Phenyl-4,4,6,6-bis(pentamethylene)-tetrahydro-3,4-furoimidazole; m.p. 230°	Methyl alcohol $5.17 \cdot 10^{-5}$	290	1500
				
3	2,2,4,4-Tetramethyltetrahydro-3,4-furo-6,7-dihydropyrazine; b.p. 75.5-75.7° (9 mm), n_D^{20} 1.4755, d_4^{20} 1.0029	Isooctane $1.69 \cdot 10^{-2}$	378	105
4	2,4-Dimethyl-2,4-diethyltetrahydro-3,4-furo-6,7-dihydropyrazine; b.p. 98.2° (6 mm), n_D^{20} 1.4789, d_4^{20} 0.9881	Isooctane $1.2 \cdot 10^{-2}$	378	105
				
5	2,2,4,4-Bis(tetramethylene)-tetrahydro-3,4-furo-6,7-dihydropyrazine; b.p. 147-148° (7 mm), n_D^{20} 1.5253, d_4^{20} 1.0900	Heptane $9.3 \cdot 10^{-3}$	373	180
6	2,2,4,4-Bis(tetramethylene)-tetrahydro-3,4-furo-6,7-dihydropyrazine; m. p. 101.5°	Heptane $2.91 \cdot 10^{-3}$	376	150
				
7	2,2,4,4-Tetramethyltetrahydro-3,4-furoquinoxaline; m.p. 101.5°	Isooctane $4.94 \cdot 10^{-4}$	323 316 309	3000 2300 2100
8	2,4-Dimethyl-2,4-diethyltetrahydro-3,4-furoquinoxaline; m.p. 110-111.5°	Isooctane $2.56 \cdot 10^{-4}$	322 314 309	4300 3300 3000
				
9	2,2,4,4-Bis(tetramethylene)-tetrahydro-3,4-furoquinoxaline; m.p. 105.5-106°	Heptane $9.12 \cdot 10^{-4}$	315 328	6300 7800

TABLE 3 (Continued)

Nos.	Structural Formula, Name and Constants	Solvent and Mole Concentration	$\lambda_{max.}$	$\epsilon_{max.}$
10	2,2,4,4-Bis(pentamethylene)-tetrahydro-2,4-furoquinoxaline; m.p. 117.2° 	Heptane $7.12 \cdot 10^{-4}$	324 318 311	9100 7400 6300
11	3-Hydroxy-5,5,7,7-bis(tetramethylene)-tetrahydro-3,4-furo-1,2,4-triazine; m.p. 194.5-195°	Methyl alcohol $3.33 \cdot 10^{-3}$	316	880
12	3-Hydroxy-5,5,7,7-bis(pentamethylene)-tetrahydro-3,4-furo-1,2,4-triazine; m.p. 214° 	Methyl alcohol $1.67 \cdot 10^{-3}$	314	1400
13	2,2,5,5-Bis(pentamethylene)-tetrahydro-3,4-furandione monosemicarbazone; m.p. 182.5-183°	Ethyl alcohol $1.38 \cdot 10^{-3}$	414 315	52 130

We also took the absorption spectra of derivatives of the same diketones: the imidazoles (which fail to have characteristic absorption bands in the investigated region), phenylimidazoles (Fig. 5), dihydropyrazines (Fig. 6), quinoxalines (Fig. 7) and the hydroxytriazines (Fig. 8). Each series of derivatives has its characteristic absorption spectra, but essential spectral changes within a series were not revealed. The absorption spectrum of the 2,2,5,5-bis(pentamethylene)-tetrahydro-3,4-furandione monosemicarbazone (Fig. 9) differs from the absorption spectra of the corresponding hydroxytriazines (Fig. 8). The $\lambda_{max.}$ and $\epsilon_{max.}$ values are given in the tables.

The spectra were taken in the Optical Laboratory of I. V. Obreimov on a Dianov-Klokov spectrophotometer.

SUMMARY

1. The absorption spectra in the ultraviolet were taken for tetraalkyltetrahydro-3,4-furandiones, tetraalkyltetrahydro-3-furanones, and some of their derivatives.

2. A study of the absorption spectra revealed that the hydration of tetrahydrofurandiones proceeds at the two carbonyl groups.

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[1] I. K. Korobitsyna, Yu. K. Yuryev and O. I. Nefedova, J. Gen. Chem. 24, 188 (1954) (T. p. 191) *.

[2] I. K. Korobitsyna, Yu. K. Yuryev, Yu. A. Cheburkov and E. M. Lukina, J. Gen. Chem. 25, 734 (1955)(T.p. 699)*.

[3] T. I. Temnikova and P. A. Tikhomolov, J. Russ. Phys.-Chem. Soc. 62, 1217 (1930); P. A. Tikhomolov and A. E. Druzhinin, J. Gen. Chem. 7, 869 (1937); V. D. Yasnopolsky, J. Gen. Chem. 18, 1789 (1948).

[4] Luthy, J. Phys. Chem. 107, 285 (1924); Lardy, J. Phys., 21, 281 (1924).

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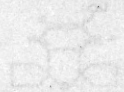
* T. p. = C. B. Translation pagination.

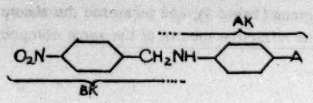


SEPARATED CHROMOPHORE SYSTEMS

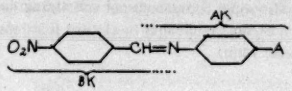
XXIX. COMPARATIVE SPECTROSCOPIC STUDIES OF 4-NITROBENZYLIDENE AND 4-NITROBENZYL DERIVATIVES OF AROMATIC AMINES

V. A. Izmailsky and E. A. Smirnov

As early as 1937 [1] we stated that the 4-nitrobenzyl derivatives of aromatic amines of general formula (I) have a deeper color than the corresponding 4-nitrobenzylidene derivatives (azomethines) of general formula (II), where A is one of the electron donor groups: $-OCH_3$, $-OH$, $-N(CH_3)_2$.



(I)

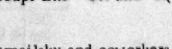


(II)

For example, p'-$O_2NC_6H_4CH_2NHC_6H_4OCH_3$-p is red [2], while its corresponding nitrobenzylidene derivative is only golden-yellow [3]; p'-$O_2NC_6H_4CH_2NHC_6H_4OH$-p has a reddish-brown color [4], while its corresponding azomethine is yellowish-brown [5]. Later it was established that the dinitrobenzyl derivatives are even more deeply colored, and the considerable theoretical interest of these compounds was indicated [6].

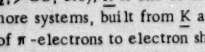
All of these facts are in contradiction: first, with the basic assumption of the chromophore theory, in accord with which the reduction of the unsaturated chromophore group (in the given case $-CH=N-$ into $-CH_2NH-$) should lead to color reduction for the compound; second, with the basic assumptions of the generally accepted theory of color, in accord with which the condition of color is associated with the presence of a general conjugation chain, where for the appearance of color it is necessary that the chromophore groups present in the compound, electrophilic groups like $-NO_2$ and electron donor groups like $-OH$ and $-N(CH_3)_2$, be linked with each other through a compact chain of conjugated atoms.

The extensive studies of V. A. Izmailsky and coworkers (for generalizations – see [7, 8, 9]) revealed that the nitrobenzylarylamines are not exceptions in this respect. At present an extremely large number of compounds have been synthesized, the color of which cannot be explained by the old theories of associating color with structure. These compounds, to which we have given the name "compounds with separated chromophore systems", are structurally of the general type (III), where K is the conjugated system (specifically – the benzene ring); B is the electrophilic chromophore group (for example, $-NO_2$, $>CO$, etc); A is one of the electron donor groups: $-OH$, $-OCH_3$, $-N(CH_3)_2$, etc; AK and BK are complex chromophore systems, built from K and A or K and B; Q is a group, breaking the conjugation (not leading with the aid of π-electrons to electron shifts and operating on the chain of atoms within the molecule, i.e., endomolecularly; for (III) it is the $-CH_2NH-$ group).*



(III)

* Nitrobenzyl derivatives can be regarded as compounds having the general formula (IV), which, however, is essentially a particular case of the more general formula (III) (the first donor group $-NH-$ is a component of Q):



(IV)

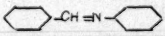
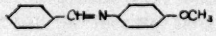
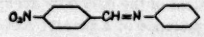
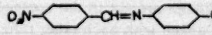
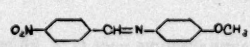
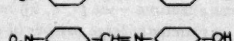
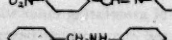
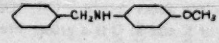
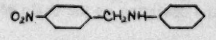
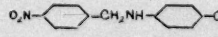
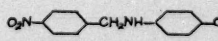
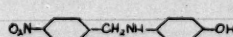
The basic factor determining the color of similar types of compounds in the solid state, as was shown by us on a large number of newly synthesized compounds, is the direct reaction of the electrophilic AK and electron donor BK systems with the aid of external field forces (exomolecular forces [8]). We still do not have a conclusive answer to the question of just where this exoreaction is an intermolecular manifestation of the external field or where it is intramolecular; apparently, it is most frequently intermolecular, but in certain cases it can also be intramolecular, and specifically, when chain bending is possible. In addition, the possibility of some contribution by endomolecular reaction should be taken into consideration.

The purpose of the present investigation was to study this problem by way of comparing the absorption and reflection spectra of the indicated two series of compounds and to elucidate the influence on the spectral pattern that is shown when groups capable of leading to conjugation are substituted by groups that rupture the conjugation of the π-electron chain, in the given case the substitution of the $-CH=N-$ group by the $-CH_2NH-$ group. This should also help solve another problem, namely: are groups of the type of $-N=N-$, $-CH=N-$, and $-CH=CH-$ basic chromophore groups in the molecule, as is assumed by a number of authors [10, 11], or does their role reduce to the formation of a general conjugation chain and modification of the chromophore effects, arising as the reaction result of the peripheral groups: the electrophilic $-NO_2$ and the electron donor group $-OH$, $-N(CH_3)_2$, $-OCH_3$, etc., forming complex chromophore systems with their conjugated systems.

For this we synthesized a number of p-nitrobenzylidene derivatives and their corresponding p-nitrobenzyl analogs, and also some compounds not containing the nitro group (Table 1), and measured the absorption spectra of all of our synthesized compounds in alcohol solutions, and the reflection spectra of the same compounds taken as solids (in powder form).

TABLE 1

Color Comparison of Benzylidene and Benzylamine Derivatives

Expt. No.	Compound formulas	Color of compound	
		As crystals	As powder
1		Almost colorless	Colorless
2		Slightly greenish	Colorless
3		Yellow	Light yellow
4		Yellow	Light yellow
5		Golden-yellow	Orange-yellow
6		Yellowish-brown	Brownish-orange
7		Colorless	Colorless
8		Colorless	Colorless
9		Intensely yellow	Yellow
10		Orange	Orange-yellow
11		Red	Reddish-orange
12		Reddish-brown	Brownish-red
13		Intensely yellow	Yellow

Absoprtion Spectra of p-Nitrobenzylidene Derivatives

All of the absorption curves of the nitrobenzylidene derivatives (Fig. 1) are first of all characterized by the presence of a well defined long wave length band (α-band). This band is also retained for nitrobenzylideneaniline (Curve 3), i.e., for compounds not containing the electron donor group (A), and in like manner for compounds in which the nitro group is absent and the electron donor group is present (Curve 2, Fig. 2). Only in the simultaneous absence of both groups, i.e., for benzylideneaniline, does this band almost completely disappear; its presence is manifested only as a slight projection in about the 300 mμ region (Curve 1, Fig. 2). The α-band position is linked with the character of the electron donor group, and in measure with increase in the donor properties of the group ($-CH_3 < -OCH_3 < -OH$) its maximum is shifted toward the longer wave lengths: at 18.5 mμ in passing from $-CH_3$ to $-OCH_3$ and at 6 mμ in passing from $-OCH_3$ to $-OH$. At the same time the absorption intensity is also increased somewhat. Removal of the donor group from the compound leads to hypsochromic shifting of the α-band (Table 2 and Fig. 1), the value of which depends on the relative "strength" of the removed electron donor group: at 17 mμ when the CH_3 group is removed, at 36 mμ for the OCH_3 group, and at 42 mμ for the OH group. A similar effect is shown when the nitro group is removed from the compound with retention of the electron donor group (Curves 5 and 2 in Fig. 2, Table 3): for compound 2, devoid of nitro group, the α-maximum when compared with compound 5, containing a nitro group, is shifted by 42 mμ toward the shorter wave lengths. Removal of the nitro group from p-nitrobenzylideneaniline leads to almost complete α-band disappearance (Curves 3 and 1 in Fig. 2, Table 3). The shifting of the α-maximum is accompanied by shifting of all of the branches of the curve lying in the visible portion of the spectrum, the value of which can be used to characterize the absorption shift limits at log $\epsilon = 2$ (Tables 2 and 3).

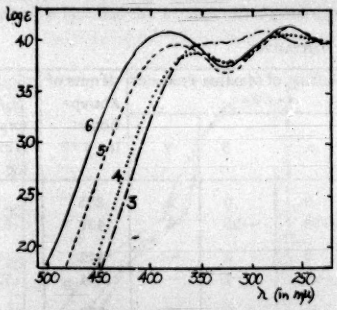


Fig. 1. Absorption curve of nitrobenzylidene Derivatives.
6) p-$O_2NC_6H_4CH=NC_6H_4OH$-p,
5) p-$O_2NC_6H_4CH=NC_6H_4OCH_3$-p,
4) p-$O_2NC_6H_4CH=NC_6H_4CH_3$-p,
3) p-$O_2NC_6H_4CH=NC_6H_5$.

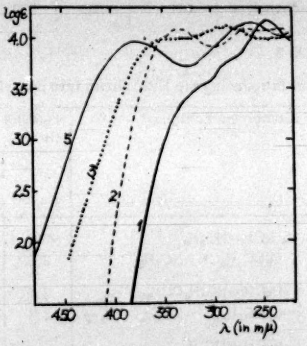


Fig. 2. Absorption curve for benzylidene and nitrobenzylidene Derivatives.
5) p-$O_2NC_6H_4CH=NC_6H_4OCH_3$-p,
3) p-$O_2NC_6H_4CH=NC_6H_5$,
2) $C_6H_5CH=NC_6H_4OCH_3$-p,
1) $C_6H_5CH=NC_6H_5$.

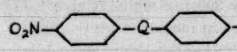
The presence of α-bands for all of the benzylideneanilines is unconditionally associated with the presence in them of a compact conjugated chain and its structure. This common conjugation chain is the vehicle of electron displacements, determined by both the electrophilic group $-NO_2$ and the electron donor groups A. Basically, the α-band determines the visible color of the solutions of the examined compounds.

In addition to the basic α-band, all of the nitrobenzylideneanilines have a second well-defined absorption band, lying in the shorter wave length region (β-band). For p-nitrobenzylideneaniline this band lies at 290 mμ. When even such a weak electron donor group as $-CH_3$ is introduced into the compound the β-band is hypsochromically shifted to 267 mμ. The introduction into the p-nitrobenzylideneaniline molecule of the typical electron donor groups $-OCH_3$ and $-OH$ causes further hypsochromic shifting of this band, but only very slightly, by 4-4.5 mμ. As a result, an interesting rule is observed: whereas in the augmenting of the electron donor properties of the groups ($-H < -CH_3 < -OCH_3 < -OH$) $\alpha\lambda_{max}$ suffers constant bathochromic shifting [+ 17, + 36, + 42 mμ (Table 2)],

under the same conditions $\beta\lambda_{max.}$ is hypsochromically shifted in the opposite direction, in which connection the value of this shifting is but slightly dependent on the donor strength properties of the groups: −23 mμ for $-CH_3$, −27 mμ for $-OCH_3$ and −27.5 mμ for the −OH group.

TABLE 2

Influence of Structure of Bonding Group Q and Electron Donor Group A on the Light Absorption Spectra for Compounds of Type



Nos.	Group Structures		Position of Maxima (in mμ)			Shifting of Maxima Produced by A			Limits of Absorption at log ε = 2	Shifting of Absorption Limits at log ε = 2
	Q	A	α	β	γ	α	β	γ		
3 •	−CH=N−	−H	338	290	−	0	0	−	438	0
4	−CH=N−	$-CH_3$	355	267	−	+ 17	−23	−	448	+ 10
5	−CH=N−	$-OCH_3$	374	263	−	+ 36	−27	−	474	+ 36
6	−CH=N−	−OH	380	262.5	−	+ 42	−27.5	−	494	+ 56
9	$-CH_2NH-$	−H	~332	270	246	0	0	0	408	0
10	$-CH_2NH-$	$-CH_3$	~334	270	248	+ 2	0	+ 2	417	+ 9
11	$-CH_2NH-$	$-OCH_3$	~345	264	248	+ 13	− 6	+ 2	421	+ 13
12	$-CH_2NH-$	−OH	~350	270	246	+ 28	0	0	446	+ 38

TABLE 3

Effect of Introducing the Nitro Group into Benzylidene and Benzyl Derivatives

Nos.	Compound Formulas	Position of Maxima (in mμ)			Shifting of Maxima Produced by ••			Limits of Absorption at log ε = 2	Shifting of Absorption Limits at log ε = 2
		α	β	γ	α	β	γ		
1 •	$C_6H_5CH=NC_6H_5$	~300	~265	244	0	0	0	375	0
3	$p\text{-}O_2NC_6H_4CH=NC_6H_5$	338	290	240	~+38	~+25	−4	438	+63
2	$C_6H_5CH=NC_6H_4OCH_3\text{-}p$	332	264	−	0	0	−	402	0
4	$p\text{-}O_2NC_6H_4CH=NC_6H_4OCH_3\text{-}p$	374	263	−	+42	−1	−	474	+72
7	$C_6H_5CH_2NHC_6H_5$	−	295	248	−	0	0	323	0
9	$p\text{-}O_2NC_6H_4CH_2NHC_6H_5$	~332	270	246	−	−25	−2	408	+85
8	$C_6H_5CH_2NHC_6H_4OCH_3\text{-}p$	~311	−	245	0	−	0	346	0
11	$p\text{-}O_2NC_6H_4CH_2NHC_6H_4OCH_3\text{-}p$	~345	264	248	~+34	−	+3	421	+75

It must be assumed that the β-band is the composite result of two separate bands, determined by the presence, on the one hand, of the electrophilic system (BK), and on the other hand, of the electron donor system (AK). In the absence of the supplementary donor group (A) its position (290mμ) is basically determined by the electrophilic system (Curve 3, Fig. 2), and in the absence of the nitro group−mostly by the electron donor system (262-266 mμ, Curve 2, Fig. 2). With the simultaneous presence of both groups, the electron donor group exerts the greater influence on the position of the β-band (Curve 5, Fig. 2).

Absorption Spectra of Nitrobenzyl Derivatives

In examining the absorption curves of nitrobenzyl derivatives (Fig. 3) attention is first of all attracted to the close resemblance in the position of these curves, despite a difference in the donor groups; and second, that the α-band, which, for the nitrobenzylidene derivatives has a well defined maximum at ε of the order of 7600-12,200,

• The numbers correspond to Table 1.

•• Nos. 1 and 3, 2 and 4, 7 and 9, and 8 and 11 are compared.

appears here only as a shallow step at a much lower ϵ value (~700) and its position can be determined only approximately. The latter circumstance can be regarded as evidence that there is reaction between the electrophilic and electron donor systems in the solutions of nitrobenzyl derivatives; however, this reaction is realized to a considerably lesser degree than for the azomethines. The reason for this must first of all be sought in the fact that for the azomethines reaction between the systems can be realized not only intermolecularly, but also for the most part intramolecularly, due to endomolecular forces by way of the compact conjugated chain, and, consequently, is independent of whether the substance is found in the dissolved or solid state. For nitrobenzyl derivatives, due to the presence of the group $-CH_2NH-$, not containing π-electrons, this reaction for the most part can be realized intermolecularly and, consequently, in solution it proceeds to a considerably lesser degree than for the same substance in the solid state.

It could further be assumed that the appearance of the α-band for nitrobenzyl derivatives is the result of traces of the azomethine being present in the benzyl derivative, which impurity is formed in the preparation of the compound due to oxidation of the nitro group. However, the following facts stand opposed to such a theory: 1) the extremely careful purification to which the compound was subjected; and 2) the presence of the same band for β-(4-nitrophenyl)-ethylaniline (Compound No. 13, Table 1 and Fig. 5), where the bonding link is the $-CH_2CH_2NH-$ group, and where, consequently, the formation of the azomethine is in general impossible.

If it is considered that at a concentration of 10^{-4} M the intermolecular reaction (with the aid of external forces) can develop only insignificantly, as was shown by the studies of Izmailsky and Gusev on molecular complexes of type (BK + AK) [12], and that the α-bond for nitrobenzyl derivatives lies in approximately the same region as for the azomethines, then it might be thought that this band for nitrobenzyl derivatives is the result of the influence of a special form of conjugation through the agency of the CH_2- and NH-groups, found linked in the group $-CH_2NH-$. However, it seems to us that the presence of this band for β-(4-nitrophenyl)-ethylaniline makes all the more probable the postulation that this band to a considerable degree is the result of exomolecular reactions in solution, despite the fact that the measurements were made at low solution concentrations (10^{-4} and 10^{-5} mole).

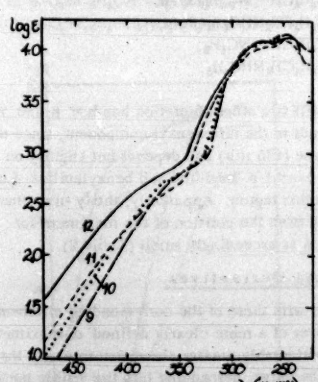


Fig. 3. Light absorption curves for nitrobenzyl derivatives.
12) p-$O_2NC_6H_4CH_2NHC_6H_4OH$-p,
11) p-$O_2NC_6H_4CH_2NHC_6H_4OCH_3$-p,
10) p-$O_2NC_6H_4CH_2NHC_6H_4CH_3$-p,
9) p-$O_2NC_6H_4CH_2NHC_6H_5$.

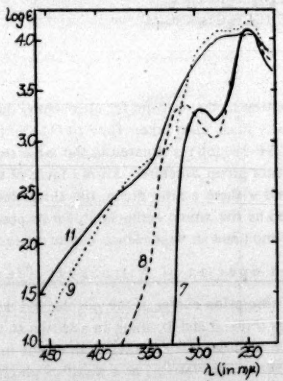


Fig. 4. Light absorption curves for benzyl and nitrobenzyl derivatives.
11) p-$O_2NC_6H_4CH_2NHC_6H_4OCH_3$-p,
9) p-$O_2NC_6H_4CH_2NHC_6H_5$,
8) $C_6H_5CH_2NHC_6H_4OCH_3$-p,
7) $C_6H_5CH_2NHC_6H_5$.

The final solution to this problem can only be found on the basis of additional experimental studies.

The bathochromic shifting of $\alpha\lambda_{max.}$, observed when additional donor groups (A) are introduced into the nitrobenzylaniline molecule, is less than when the same groups are introduced into the nitrobenzylideneaniline molecule (Table 2). This can be explained by the fact that for all of the nitrobenzyl derivatives, in addition to the donor group A ($-CH_3$, $-OCH_3$ or $-OH$, appearing as the second donor group), there already exists the first donor

group –NH, in which connection this group possesses stronger donor properties than the second, and consequently the influence of the second (in our case the weaker) donor group A is less developed. This explains the considerably closer resemblance existing for the absorption curves in the nitrobenzyl derivative series when compared with the azomethines.

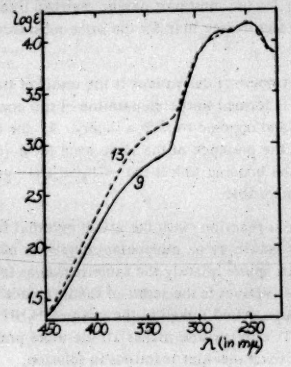


Fig. 5. Light absorption curves for nitrobenzylaniline and β-(4-nitrophenyl)-ethylaniline.
9) p-$O_2NC_6H_4CH_2NHC_6H_5$,
13) p-$O_2NC_6H_4CH_2CH_2NHC_6H_5$.

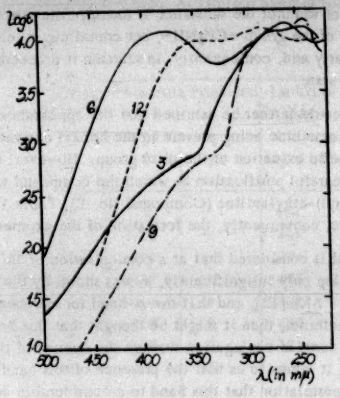


Fig. 6. Comparison of the light absorption curves for nitrobenzylidene and nitrobenzyl derivatives.
6) p-$O_2NC_6H_4CH=NC_6H_4OH$-p,
12) p-$O_2NC_6H_4CH_2NHC_6H_4OH$-p,
3) p-$O_2NC_6H_4CH=NC_6H_5$,
9) p-$O_2NC_6H_4CH_2NHC_6H_5$.

In addition to the α-band for nitrobenzyl derivatives, there exist still two other absorption bands – β and γ, which partially mask each other. The first of them (β) apparently corresponds to the nitrobenzyl component, since the maximum (254-260 mμ) is situated in the same region as for p-nitrotoluene (275 mμ) and depends but slightly on change in donor group structure. Also in favor of this is the fact that for benzyl-p-anisidine and benzylaniline, i.e., for compounds without a nitro group, the absoprtion minimum is found in this region. Apparently, the γ-maximum is determined by the amino component, for its position differs but slightly from the position of the maximum for aniline (230 mμ) and its dependence on the character of the donor group A is exceedingly small (Table 2).

Reflection Spectra of Nitrobenzylidene and Nitrobenzyl Derivatives

If the absorption curves of the nitrobenzyl derivatives are compared with those of the corresponding nitrobenzylidene analogs (Figs. 6 and 7), then, in addition to the presence for the latter of a more clearly defined α-maximum, it can also be seen that for the azomethines this maximum possesses a considerably greater absorption intensity than for the nitrobenzyl derivatives, as a result of which the whole branch of the curve, descending into the visible portion of the spectrum, proves to be situated more bathochromically for the nitrobenzylidene derivatives than for the nitrobenzyl derivatives. Consequently, if the visible color of substances is judged on the basis of their light absorption curves, then it should be expected that the nitrobenzylidene derivatives will possess in the solid state a deeper color than their corresponding nitrobenzyl derivatives. However, actually we have the reverse situation, i.e., all of the nitrobenzylidene derivatives in the solid state prove less deeply colored than their corresponding nitrobenzyl analogs. This can easily be seen even with the naked eye, and is confirmed by the visible light reflection curves, obtained by us for all of the examined compounds with visible color. As can be seen from Figs. 8 and 9, the order in which the light reflection curves are arranged coincides exactly with the order of visually observed color change. As a result, in the given case the light reflection curves give a truer picture of the relative depth of color of the examined compounds (in the solid state) than do the light absorption curves.

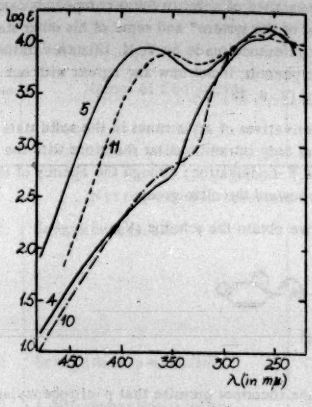


Fig. 7. Comparison of the light absorption curves for nitrobenzylidene and nitrobenzyl derivatives.

5) p-$O_2NC_6H_4CH=NC_6H_4OCH_3$-p,
11) p-$O_2NC_6H_4CH_2NHC_6H_4OCH_3$-p,
4) p-$O_2NC_6H_4CH=NC_6H_4CH_3$-p,
10) p-$O_2NC_6H_4CH_2NHC_6H_4CH_3$-p.

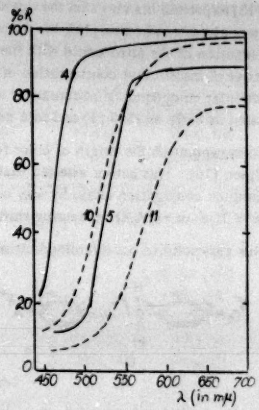


Fig 8. Light reflection curves for nitrobenzylidene and nitrobenzyl derivatives.

4) p-$O_2NC_6H_4CH=NC_6H_4CH_3$-p,
10) p-$O_2NC_6H_4CH_2NHC_6H_4CH_3$-p,
5) p-$O_2NC_6H_4CH=HC_6H_4OCH_3$-p,
11) p-$O_2NC_6H_4CH_2NHC_6H_4OCH_3$-p.

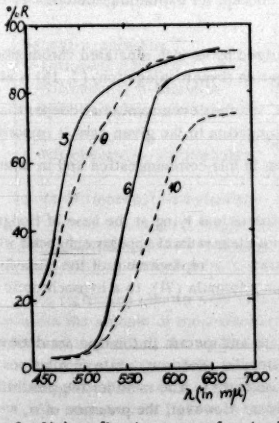


Fig. 9. Light reflection curves for nitrobenzylidene and nitrobenzyl derivatives.

3) p-$O_2NC_6H_4CH=NC_6H_5$,
9) p-$O_2NC_6H_4CH_2NHC_6H_5$,
6) p-$O_2NC_6H_4CH=NC_6H_4OH$-p,
10) p-$O_2NC_6H_4CH_2NHC_6H_4OH$-p.

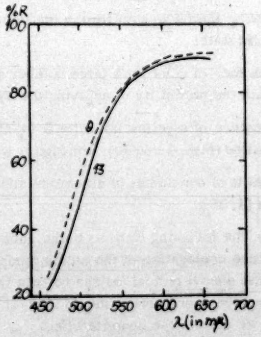


Fig. 10. Light reflection curves for nitrobenzylidene-aniline and β-(4-nitrophenyl)-ethylaniline.

9) p-$O_2NC_6H_4CH_2NHC_6H_5$,
13) p-$O_2NC_6H_4CH_2CH_2NHC_6H_5$.

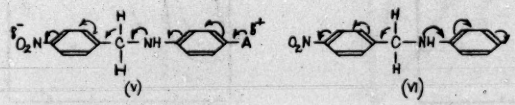
At the time that Izmailsky and Samokish studied absorption spectra in solution and reflection spectra for substances in the solid state, it was shown [7] that the conclusions on the electron structure of substances and the reason for their color, made on the basis of visual observations, are inadequate and are based on frequently contradictory spectral measurement results made in solution. Our investigations support this. The reason lies in the fact that the color of substances in the solid state is determined

not only by intramolecular, but also by extramolecular reactions, which in the presence of strongly polar chromophone systems BK and AK can lead to an entirely different effect.

Ufimtsev [13] expressed his views on the questions associated with color for the nitrobenzyl derivatives of arylamines. As was already indicated [14], his postulation that "the appearance of color in these compounds cannot be explained by reaction of the nitro-enoid with the auxo-enoid portions of the system" and some of his other statements, are the result of insufficient consideration of the literature. The reference made by V. N. Ufimtsev to the analogy with molecular compounds of nitrotoluene and amines, and also phenols, is not new and agrees with our statement, expressed as early as 1937 [1] and in a number of other papers [7, 9, 15].

An opposite viewpoint on the origin of color for the nitrobenzyl derivatives of arylamines in the solid state was expressed by Hodgson [16]. This author asserted that color is the result of only intramolecular reactions with the formation of a common conjugation chain by way of hyperconjugation (σ,π-conjugation) through the agency of the groups $-CH_2-NH-CH=$ or $-CH_2NH-$, causing shifting of the electrons toward the nitro group.

Applying this viewpoint to our examined nitrobenzyl derivatives, we obtain the scheme (V):



(V) (VI)

However, Hodgson admitted a number of errors. He started from the incorrect premise that p-nitrobenzylaniline as it were, is devoid of visible color and explained its absence by structure (VI). To the contrary, this compound has been described as a yellow [17] or orange [18] substance. Further, the formulas given for the structures of 3-(p-nitrobenzylamino)-acenaphthene and 1-(p-nitrobenzylamino)-fluorene were incorrect, as a result of which it becomes necessary to consider the deliberations made as to the transfer of influence through the group $-CH_2-NH-CH=$ to be without basis. Finally, it should be mentioned that all of Hodgson's considerations of electron shifting were based on visual color determinations for compounds in the solid, crystalline state.

The following facts also confirm the inadequate nature of Hodgson's concept for explaining the color of compounds in the solid state:

1) the presence of color for a large number of the compounds synthesized by us with separated chromophore systems, for which the possibility of applying the hypothesis of σ,π-conjugation (hyperconjugation) [7, 19] is absent;

2) the presence of a yellow color for β-(4-nitrophenyl)-ethylaniline, which is even somewhat deeper than for 4-nitrobenzylaniline (Figs. 5 and 10), although it would seem that σ,π-conjugation in the given case is impossible;

3) the results of our studies of absorption and reflection spectra, given in this communication and in other communications [1, 19];

4) finally, the following testifies to the anomalous nature of the considerations lying at the base of Hodgson's formula (VI): since conjugation of the amino group with an aromatic multinuclear radical appears enhanced when compared with the phenyl radical (as can be seen from the absorption spectra), replacement of the phenyl radical by acenaphthene or fluorene should lead, if we proceed from Hodgson's formula (VI), to a hypsochromic effect. Actually, we observe the opposite effect.

Our investigations have shown without doubt that color in the solid state and spectra in solution are determined by different causes. Color in the solid state is basically the result of exomolecular reactions, while in solutions both endomolecular and exomolecular reactions can prevail. Here it becomes necessary to also consider the possibility of the presence of σ,π-conjugation for the CH_2 group under certain conditions. However, the presence of σ,π-conjugation cannot be based on color observations of substances in the solid state, as was done by Hodgson. In judging the role played by the NH- group, it becomes necessary to take into consideration the studies of V. A. Izmailsky and A. M. Simonov [32].

As a result, both possible forms of reaction – exomolecular and endomolecular – should be taken into consideration, which reactions are manifested to different degree, depending on the conditions.

EXPERIMENTAL

All of our studied compounds are described in the literature; consequently, here we will limit ourselves to indicating the purification methods used by us for the synthesized compounds, and to presenting the melting points obtained by us and those given in the literature (Table 4).

TABLE 4

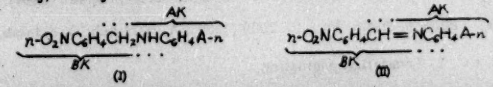
Nos.	Names of Compounds	Substance Purification by Crystallization	Melting Point		Solution Concentration taken for Spectroscopy
			Found	From the Literature	
	Nitrobenzylidene and Benzylidene Derivatives of Aromatic Amines				
1	Benzylideneaniline	Twice from dilute alcohol	49-50° (Second melting 54)	48-49°[24] 52-53 [25] 54 [26 (Second melting 54 [24])	10^{-2} and 10^{-3} M.
2	Benzylidene-p-anisidine	Once from alcohol and 3 times from methanol	72	72 [22]	10^{-3} M.
3	4-Nitrobenzylideneaniline	Twice from methanol	92.5	93 [21]	$0.5 \cdot 10^{-4}$ M.
4	4-Nitrobenzylidene-p-toluidine	Twice from alcohol	124	124.5[20]	$0.5 \cdot 10^{-4}$ M.
5	4-Nitrobenzylidene-p-anisidine	Twice from alcohol	139.5	139 [3]	$0.5 \cdot 10^{-4}$ M.
6	4-Nitrobenzylidene-p-aminophenol	Thrice from alcohol	169.5	168.5[5]	10^{-5} M.
	Nitrobenzyl and Benzyl Derivatives of Aromatic Amines				
7	Benzylaniline	From gasoline (after vacuum-distillation)	36°	36°[29]	$2 \cdot 10^{-3}$ and $2 \cdot 10^{-4}$ M.
8	Benzyl-p-anisidine	Thrice from methanol	51.5	52 [28]	10^{-2} and 10^{-3} M.
9	4-Nitrobenzylaniline	Thrice from alcohol	71.5	72 [18]	10^{-3} M.
10	4-Nitrobenzyl-p-toluidine	Twice from alcohol	68	68 [27]	10^{-3} M.
11	4-Nitrobenzyl-p-anisidine	Thrice from alcohol and once from methanol	95.5-96.5	96-97[2]	10^{-3} and 10^{-4} M.
12	4-Nitrobenzyl-p-aminophenol	From chloroform and from gasoline	114-115	114-115[4]	10^{-3} and 10^{-4} M.
13	β-(4-Nitrophenyl)-ethylaniline	From alcohol	69	69 [30]	10^{-3} M.

The absorption spectra were taken with a Beckmann spectrophotometer. As solvent, we used pure alcohol, previously distilled through a fractionating column.

The reflection spectra were taken with the apparatus built by E. V. Shpolsky [31]. A photoelement was used to measure the amount of monochromatic light (different wave lengths) reflected by the substance as a very fine powder, and in parallel, the amount of light reflected by magnesium oxide. On the basis of the obtained data, the percent of reflected light (% R) for each of the monochromatic rays was found, and then the curves were constructed, where along the abscissa the wave lengths (in mμ) were plotted, and along the ordinate the percent of reflected light (% R). An incandescent light bulb served as the light source.

SUMMARY

1. On the basis of visual observations and measuring the reflection spectra of powders, it was established that the derivatives of p-nitrobenzylaniline (I) in the solid state have a deeper color than the corresponding derivatives of p-nitrobenzylideneaniline (II) (A = −H, $-CH_3$, $-OCH_3$ and −OH).



2. However, just the reverse is observed for absorption spectra in solution: the long wave length α-maximum for the nitrobenzylidene derivatives (λ = 338, 355, 374, 380 mμ) has a more bathochromic position than for the nitrobenzyl derivatives (λ = 332, 334, 345, 350 mμ), in which connection for the latter it is expressed only as a step.

3. The deeper color in the solid state of compounds (I) is explained by the presence of a stronger electron donor system (AK) than for compounds (II), and its exomolecular reaction with the electrophilic system (BK).

4. The more hypsochromic position of the absorption curves in solution for the same compounds (I) when compared with those for (II) can be explained by disturbance to considerable degree of exomolecular reaction in solution and the absence of conjugation between $-NO_2$ and A. The absorption spectra for compounds (II) are basically determined by reaction of A and $-NO_2$ by chain conjugation.

5. The representations of Hodgson [16] relative to electron shifts in nitrobenzyl derivatives of arylamines cannot be acknowledged as being well-grounded, since he failed to take into consideration the fact that the color of these compounds in the solid state is basically the result of exomolecular reactions.

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THE PREPARATION OF SOME ETHYLENEIMINO-1,3,5-TRIAZINES

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Up to now only one member of the ethyleneiminotriazine series, namely 2,4,6-triethyleneimino-1,3,5-triazine [1], has been described in the chemical literature. This compound was obtained by reacting ethyleneimine with cyanuric chloride, where it was found that in contrast to most amines [2-5], ethyleneimine is capable of replacing all three chlorine atoms of cyanuric chloride even at room temperature.

Desiring to synthesize some ethyleneiminetriazines of interest to us, containing in the triazine cycle together with the ethyleneimine radical an aliphatic or aromatic radical, or an alkoxy or phenoxy group, we condensed ethyleneimine with 2-ethyl-4,6-dichloro-, 2,4-diphenyl-6-chloro-, 2-methoxy-4,6-dichloro, 2,4-dimethoxy-6-chloro-, 2-ethoxy-4,6-dichloro- and 2-phenoxy-4,6-dichloro-1,3,5-triazines. In all cases, the reaction proceeded smoothly at 20-25° and as a result, we were able to obtain in good yield, respectively, 2-ethyl-4,6-diethyleneimino-1,3,5-triazine (I), 2,4-diphenyl-6-ethyleneimino-1,3,5-triazine (II), 2-methoxy-4,6-diethyleneimino-1,3,5-triazine (III), 2,4-dimethoxy-6-ethyleneimino-1,3,5-triazine (IV), 2-ethoxy-4,6-diethyleneimino-1,3,5-triazine (V) and 2-phenoxy-4,6-diethyleneimino-1,3,5-triazine (VI).

(I) $R^2 = C_2H_5$; $R^4 = R^6 = CH_2CH_2N$;

(II) $R^2 = R^4 = C_6H_5$; $R^6 = CH_2CH_2N$;

(III) $R^2 = CH_3O$; $R^4 = R^6 = CH_2CH_2N$;

(IV) $R^2 = R^4 = CH_3O$; $R^6 = CH_2CH_2N$;

(V) $R^2 = C_2H_5O$; $R^4 = R^6 = CH_2CH_2N$;

(VI) $R^2 = C_6H_5O$; $R^4 = R^6 = CH_2CH_2N$;

(VII) $R^2 = R^4 = CH_2CH_2N$; $R^6 = Cl$;

(VIII) $R^2 = C_6H_5CH_2O$; $R^4 = R^6 = CH_2CH_2N$;

(IX) $R^2 = R^4 = R^6 = CH_3CHCH_2N$.

The reaction of the calculated amount of ethyleneimine with cyanuric chloride gave 2,4-diethyleneimino-6-chloro-1,3,5-triazine (VII), which condensed with sodium methylate, gave 2-methoxy-4,6-diethyleneimino-1,3,5-triazine (III), while with sodium benzylate it gave 2-benzyloxy-4,6-diethyleneimino-1,3,5-triazine (VIII).

For binding the hydrogen chloride formed in the reaction of ethyleneimine with chlorotriazines, we usually took an excess of the ethyleneimine, since the use of triethylamine, recommended for this purpose in the preparation of 2,4,6-triethyleneimino-1,3,5-triazine [1], leads to less pure condensation products.

1,2-Propyleneimine, similar to ethyleneimine, also replaces all three chlorine atoms in cyanuric chloride at room temperature. However, under these conditions the formation of 2,4,6-tri-(1', 2'-propyleneimino)-1,3,5-triazine proceeds slowly, and for satisfactory results the duration of reaction should be not less than 7 to 8 days. Of interest is the fact that the tripropyleneiminotriazine, after the first crystallization of the reaction product with m.p. ~100°, after subsequent recrystallizations from dry petroleum ether, as a rule, melts completely only if the capillary is entered into the heated melting point apparatus. The elementary analyses and molecular weight determinations of such "degraded" specimens give excellent results. After 7-28 days similar specimens melt at 104-105°, independent of how their melting points are taken. A satisfactory explanation for this phenomenon was not found.

E. H. Markachev participated in this work.

EXPERIMENTAL

2-Ethyl-4,6-diethyleneimino-1,3,5-triazine (I). To a solution of 5.2 ml of ethyleneimine in 60 ml of anhydrous benzene (6-10° and stirring) was added in drops a solution of 3.6 g of 2-ethyl-4,6-dichloro-1,3,5-triazine [6] in 40 ml of anhydrous benzene. Without ceasing to stir, the reaction solution was allowed to warm up to room temperature and then stirred for another 3 hours. After this time the Beilstein test for halogen compounds showed negative in the filtrate of a small portion of the reaction solution. The next day the filtered solution was evaporated in vacuo without heat almost to dryness; the resulting precipitate (3.4 g) was recrystallized from petroleum ether (b.p. 60-80°) and gave 2.35 g of white needle crystals with m.p. 64-65°, while evaporation of the mother liquor gave another 0.13 g of substance with m.p. 63-64°. The total yield was 64.2%. After additional recrystallization from petroleum ether, m.p. 65-65.5°.

Found %: C 56.83; H 6.93. $C_9H_{13}N_5$. Calculated %: C 56.51; H 6.85.

The substance is readily soluble in water, alcohol, chloroform, ethyl acetate and benzene. The pure substance after storage for a year at room temperature failed to change its external appearance, but its melting point was lowered 1°. The impure substance turns yellow even after standing several days.

2-4-Diphenyl-6-ethyleneimino-1,3,5-triazine (II). To a solution of 2.68 g of 2,4-diphenyl-6-chloro-1,3,5-triazine [6] in 40 ml of anhydrous benzene with vigorous stirring at 5-8° was added, dropwise, a solution of 1.5 ml of ethyleneimine in 5 ml of anhydrous benzene; stirring was continued for 3 hours at room temperature, the mixture let stand overnight, filtered, and evaporated in vacuo without heat to dryness. The yield of triazine (II) was 2.65 g (96.7%), m.p. 138-140.5°. For purification, the substance was dissolved in benzene, the filtrate evaporated nearly to dryness, the residue rubbed with petroleum ether, separated, dissolved in boiling anhydrous ether (1:120), treated with charcoal, and the filtrate evaporated in vacuo to small volume. Crystals with m.p. 144-145° were obtained.

The substance is insoluble in water, soluble in alcohol, moderately soluble in ethyl acetate, easily soluble in benzene and chloroform, and slightly soluble in petroleum ether.

Found %: C 74.54; H 4.90; N 19.89. $C_{17}H_{14}N_4$. Calculated %: C 74.42; H 5.14; N 20.44.

2-Methoxy-4,6-diethyleneimino-1,3,5-triazine (III). a) A solution of 4 ml of ethyleneimine in 48 ml of anhydrous benzene was condensed with 2.8 g of crude 2-methoxy-4,6-dichloro-1,3,5-triazine * in 31 ml of anhydrous benzene, as indicated in the preparation of (II). The methoxydichlorotriazine solution should first be filtered. After evaporation of the decanted reaction solution in vacuo to a volume of ~10 ml, the resulting precipitate was washed with anhydrous ether, air-dried, and recrystallized from anhydrous ethyl acetate (1:5). The obtained triazine (III) begins to change at 118° and melts at 119-120.5°. A second recrystallization raises the m.p. to 120-120.5°.

Found %: C 50.09; H 5.86; N 36.09. $C_8H_{11}ON_5$. Calculated %: C 49.71; H 5.74; N 36.27.

b) A hot solution of 1.18 g of 2,4-diethyleneimino-6-chloro-1,3,5-triazine** in 18 ml of anhydrous benzene was added to a solution of 0.15 g of metallic sodium in a mixture of 1.7 ml of anhydrous methyl alcohol and 0.4 ml of anhydrous benzene, the mixture boiled under reflux for 2.5 hours, and the still-hot solution suction filtered. The filtrate was evaporated in vacuo to small volume and the separated methoxydiethyleneiminotriazine (0.65 g) recrystallized from anhydrous ethyl acetate. M.p. 119-120.5°. The substance is readily soluble in water, methyl alcohol, acetone and chloroform, soluble in benzene, and difficultly soluble in ether.

2-4-Dimethoxy-6-ethyleneimino-1,3,5-triazine (IV). A solution of 3.3 g of 2,4-dimethoxy-6-chloro-1,3,5-triazine [7] in 40 ml of anhydrous benzene was condensed with 2.4 ml of ethyleneimine in 50 ml of anhydrous benzene, as indicated for the preparation of (II). The yield of the triazine (IV), purified by recrystallization from anhydrous ethyl acetate, was 2.3 g. Stout prisms with m.p. 118-119°. Evaporation of the mother liquor to small volume gave another 0.3 g of substance with m.p. 116-118°. Total yield 76%. After further recrystallization from ethyl acetate, the dimethoxyethyleneiminotriazine melts at 120-121° with previous shriveling at 119°. The substance is slightly soluble in cold water, soluble in alcohol and benzene, more difficultly soluble in ether, and readily soluble in chloroform.

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* 2-Methoxy-4,6-dichloro-1,3,5-triazine was synthesized according to [7] yield 69-70%, m.p. 88-89°. After recrystallization from hexane (1:30), m.p. 89-91°. According to the data of the mentioned authors, the yield of crude substance with m.p. 87-89° is 58%, and if the yield is recalculated on the indicated weight in grams, it is a total of 29.2%.

** The preparation of the diethyleneiminochlorotriazine is described below.

Found %: C 46.24; H 5.49; N 30.48. $C_7H_{10}O_2N_4$. Calculated %: C 46.13; H 5.53; N 30.77.

2-Ethoxy-4,6-diethyleneimino-1,3,5-triazine (V). The necessary 2-ethoxy-4,6-dichloro-1,3,5-triazine was prepared the same as 2-methoxy-4,6-dichloro-1,3,5-triazine [7]: into a mixture of 11.1 g of freshly distilled cyanuric chloride, 87 ml of anhydrous alcohol, and 7.5 ml of water with good stirring at room temperature was gradually sifted 10.2 g of sodium bicarbonate; then stirring was continued at 30° until carbon dioxide ceased to be evolved (45 minutes), the mixture cooled to room temperature, and 150 ml of water added; here an oil separated, which solidified on cooling with ice and salt. The solidified oil was separated, washed with water, dried in a vacuum-desiccator, dissolved in 34 ml of hexane (charcoal), the filtrate partially evaporated in vacuo, and cooled to –10 to –12°. The yield of the ethoxydichlorotriazine was 6.7 g (57.5%); m.p. 30-32°. For analysis, the substance was recrystallized again, as indicated above. M.p. 31.5-32.5°.

Found %: C 30.92; H 2.86; Cl 36.43. $C_5H_5ON_3Cl_2$. Calculated %: C 30.93; H 2.60; Cl 36.56.

A solution of 5.4 g of the ethoxydichlorotriazine in 55 ml of anhydrous benzene was condensed with 7 ml of ethyleneimine in 83 ml of anhydrous benzene, as described for the preparation of (II). The residue, obtained after the removal in vacuo of the benzene from the reaction solution filtrate, was dissolved in 42 ml of boiling ethyl acetate (charcoal), the filtrate evaporated to small volume, and the separated substance recrystallized from 130 ml of hexane; prismatic needles with m.p. 75.5-76.5°. Yield of 2.9 g (50.3%). The substance is readily soluble in water, alcohol, benzene and chloroform.

Found %: C 52.22; H 6.19; N 34.0. $C_9H_{13}ON_5$. Calculated %: C 52.14; H 6.32; N 33.81.

2-Phenoxy-4,6-diethyleneimino-1,3,5-triazine (VI). A solution of 8.15 g of 2-phenoxy-4,6-dichloro-1,3,5-triazine [6] in 100 ml of anhydrous benzene was condensed with 7.5 ml of ethyleneimine in 66 ml of anhydrous benzene, as described for the preparation of 2,4-diphenyl-6-ethyleneimino-1,3,5-triazine. After the removal in vacuo without heat of the benzene from the reaction solution filtrate, there remained a crystalline residue permeated with oil, which was triturated with dry ether, separated, and dissolved in boiling anhydrous ether (charcoal). The substance was obtained from the partially evaporated filtrate as needle crystals with m.p. 101-103°. Yield about 50%. After two additional recrystallizations from anhydrous ethyl acetate, m.p. 104-105°. The substance is slightly soluble in water, readily soluble in alcohol, chloroform and benzene, and difficultly soluble in ether and petroleum ether.

Found %: C 61.31; H 5.28; N 27.68. $C_{13}H_{13}ON_5$. Calculated %: C 61.14; H 5.13; N 27.45.

2-4-Diethyleneimino-6-chloro-1,3,5-triazine (VII). To a solution of 3.7 g of cyanuric chloride in 54 ml of anhydrous benzene with stirring at 5-7°, was slowly added a solution of 4.2 g of ethyleneimine in 40 ml of anhydrous benzene. Then, with stirring, the temperature of the reaction solution was permitted to rise to room temperature, stirring was continued for another 3 hours, and the whole let stand overnight. The next day the mixture was heated under reflux for 30 minutes, filtered, and the filtrate evaporated in vacuo without heat to dryness. The residue was triturated with ether, filtered, and recrystallized from 65 ml of anhydrous ethyl acetate (charcoal). Yield of (VII) 49.3%. After a second recrystallization from anhydrous ethyl acetate, the substance melted with decomposition at 128° with rapid heating, toward the end at a rate of 4° per minute, and at 140° if the capillary was entered into the apparatus at 135°. White needle crystals, readily soluble in acetone and chloroform, moderately soluble in benzene, difficultly soluble in water, and slightly soluble in ether and petroleum ether.

Found %: C 42.89; H 4.08; N 35.70; Cl 17.82. $C_7H_9N_5Cl$. Calculated %: C 42.52; H 4.08; N 35.45; Cl 17.95.

2-Benzyloxy-4,6-diethyleneimino-1,3,5-triazine (VIII). As usual, 0.2504 g of metallic sodium was comminuted by heating to the boil with 4.7 ml of xylene, to the cooled mixture was added 1.12 ml of anhydrous benzyl alcohol, and the whole heated in a glycerine bath for 2 hours at ~70° (in the bath)[8]. To the resulting thick slurry was added a hot solution of 1.67 g of 2,4-diethyleneimino-6-chloro-1,3,5-triazine in 27 ml of anhydrous benzene, the mixture boiled for 2 hours at ~100° (in the bath), the still warm solution filtered from the separated sodium chloride and granules of unreacted metallic sodium, the precipitate washed with anhydrous benzene, and the combined filtrates evaporated in vacuo without heat to dryness. The residue was triturated with ether and filtered. Yield 1.22 g (53.6%). After recrystallization from anhydrous ethyl acetate, m.p. 127.5-128.5°. The substance is readily soluble in chloroform, moderately soluble in benzene, slightly soluble in alcohol, and very slightly soluble in water, ether and petroleum ether.

Found %: C 62.70; H 5.78; N 25.97. $C_{14}H_{15}ON_5$. Calculated %: C 62.42; H 5.62; N 26.02.

2,4,6-Tri-(1',2'-propyleneimino)-1,3,5-triazine (IX). To a solution of 12 ml of 1,2-propyleneimine in 60 ml of anhydrous benzene at not above 16° and with stirring, was added a solution of 4.4 g of cyanuric chloride in 48 ml of anhydrous benzene. With periodic shaking, the mixture remained in a stoppered flask for 8 days, then it was filtered and the filtrate was evaporated in vacuo without heat to dryness. The residual semisolid mass was triturated with 50 ml of petroleum ether (b.p. 60-80°) and the obtained powder, containing halide impurities, was recrystallized from petroleum ether (b.p. 60-80°). Yield 2.07 g. Needles with m.p. 99-100°. After two recrystallizations from the same solvent, m.p. 104-105° (the capillary was entered into the apparatus at 100°). The substance is readily soluble in the cold in water, chloroform, ethyl acetate and benzene.

Found %: C 58.54; H 7.20. M 233.5. $C_{12}H_{18}N_6$. Calculated %: C 58.49; H 7.37; M 246.18.

2-Isopropyl-4,6-dichloro-1,3,5-triazine, synthesized by the method of Hirt, Nidecker and Berchtold [6], has b.p. 92° at 14 mm, and not 101-104° at 12 mm, as indicated by these authors.

Found %: Cl 36.97. $C_6H_7N_3Cl_2$. Calculated %: Cl 36.94.

SUMMARY

1. The condensation of ethyleneimine with alkyl-, aryl- and alkoxy-substituted mono- or dichloro-1,3,5-triazines gave the corresponding alkyl-, aryl- and alkoxy-substituted mono- or diethyleneimino-1,3,5-triazines.

2. The reaction of sodium methylate and benzylate with 2,4-diethyleneimino-6-chloro-1,3,5-triazine gave, respectively, 2-methoxy- and 2-benzyloxy-4,6-diethyleneimino-1,3,5-triazine.

3. The condensation of 1,2-propyleneimine with cyanuric chloride gave 2,4,6-tri-(1',2'-propyleneimino-1,3,5-triazine.

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OXIDATION OF ORGANIC COMPOUNDS

XI. THE CATALYTIC OXIDATION OF p-CYMENE IN THE LIQUID PHASE*

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Recently, much attention has been given by investigators to processes for the liquid phase catalytic oxidation of hydrocarbons with atmospheric oxygen [1-3], making it possible to obtain such valuable oxygen-containing compounds as alcohols, ketones, aldehydes, acids and others without the use of expensive oxidizing agents. Some of these processes have already found practical application [3-5].

The reactions for the liquid phase catalytic oxidation of paraffin, petrolatum and other petroleum products [6-13] with the purpose of obtaining fatty acids and hydroxy acids have received wide attention. The liquid phase catalytic oxidation of aromatic hydrocarbons has also been studied. In numerous papers it was shown that salts of different organic acids with manganese, cobalt, nickel, iron, chromium, vanadium, lead or other metals can be used as catalysts. The oxidation products are usually different aromatic alcohols [16], carbonyl compounds [5,14,15,18] and acids [3, 17,19].

A number of papers are devoted to a study of the liquid phase oxidation of p-cymene. Senseman and Stubbs [20] studied the liquid phase oxidation of p-cymene with oxygen at 140-170° in the presence of manganese acetate or toluate, or the oxides of chromium, cobalt, iron, nickel, copper and manganese. Among the reaction products were identified p-toluic and terephthalic acids, p-tolyl methyl ketone, formaldehyde, water and carbon dioxide.

The oxidation of p-cymene proceeds in similar manner also in the presence of cobalt stearate catalyst [21]. Here, in addition to the above enumerated oxidation products, are formed p-acetylbenzoic acid and traces of p-cresol. Also, some dicymyl-8,8-peroxide with m.p. 57° was isolated.

In some patents [22,23] it is mentioned that the oxidation of p-cymene in the presence of cobalt or manganese salts of cumic or acetic acid, and also in the presence of manganese dioxide or the salts and oxides of certain heavy metals, at 45-125°, i.e., at comparatively low temperatures, yields cumic acid and p-tolyldimethylcarbinol. The possibility of forming hydroxyl compounds in the liquid phase oxidation of p-cymene in the presence of a copper or iron spiral is also indicated by Booser and Fenske [24].

In most of the above presented studies the basic attention has been devoted to the practical side of the problem – the elucidation of the optimum operating conditions. From the viewpoint of studying its mechanism, the reaction for the catalytic oxidation of alkylbenzenes in the liquid phase has been studied to very slight degree.

The purpose of this study was to elucidate the reaction mechanism for the liquid phase catalytic oxidation of alkylbenzenes with oxygen at 170-172°. p-Cymene was chosen as the study subject. As catalysts were studied the manganese, cobalt and copper salts of p-toluic and terephthalic acids, manganese dioxide and naphthenate, and also spun glass and crushed Pyrex glass. The duration of reaction and the rate of oxygen passage were varied in the different experiments. The obtained results are given in the Table.

The main reaction products were p-tolyl methyl ketone and p-toluic acid, and also tarry products of composition (in %): C 82.98, H 7.53, O 9.49. Cumic and terephthalic acids, acetone and 1,1,2,2-tetramethyl-1,2-di-p-tolylethane (dicymyl) were present in small amounts. p-Cresol and organic peroxides were present as traces.

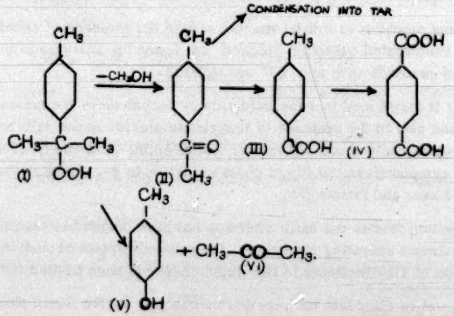
The most active oxidation catalyst proved to be manganese toluate. With it the yields of p-toluic and p-tolyl methyl ketone were respectively 26 and 4 %. Other catalysts, and especially copper toluate, proved to be less active. However, the yield of p-tolyl methyl ketone in these cases was frequently equal, and at times even higher, than the yield of p-toluic acid.

* Communication X cf.: Bull. Acad. Sci. Kazak SSR, Chemical Series, No. 9 (1954).

Expt. No.	Name and amount of catalyst * (in %)		Duration of reaction (in hours)	Rate of oxygen passage (in liters/hour)	Yield (in percent of theoretical on taken p-cymene)			Yield (in percent on weight of taken p-cymene)	
					p-Tolyl methyl ketone	p-Toluic acid	Dicymyl	Water	Tarry products
1	Manganese toluate	1.0	11	30	4.1	26.3	Traces	14.0	27.8
2	Manganese toluate	0.5	11	30	3.3	23.1	Traces	13.1	28.8
3	Cobalt toluate	0.5	11	30	3.9	7.9	Traces	8.1	22.8
4	Copper toluate	0.5	11	30	7.5	3.3	Traces	5.2	8.8
5	Manganese terephthalate	0.5	11	30	12.2	6.9	Traces	7.4	27.2
6	Manganese naphthenate	0.5	11	30	11.6	6.6	Traces	12.4	18.8
7	Manganese naphthenate	2.0	15	4.0	3.0	3.3	Traces	Not determined	Not determined
8	Manganese dioxide	0.5	11	30	15.0	3.6	1.6	4.8	30.0
9	Manganese dioxide	0.5	11	1.6	5.7	1.9	3.3	3.5	14.0
10	Crushed pyrex glass		20	10	26.3	–	5.4	Traces	2.7
11	Spun glass		20	10	7.0	–	8.5	Traces	6.5

The qualitative composition and quantitative ratios of the reaction products give basis to assume that although the catalysts investigated by us possess different activity, the oxidation of the p-cymene in all cases proceeds by the same mechanism, which mechanism can be satisfactorily explained from the viewpoint of the A. N. Bakh peroxide theory and the N. N. Semenov theory of chain processes.

The initial oxidation stage of the p-cymene molecule under the studied conditions should, apparently, be considered to be the predominant formation of p-cymene hydroperoxide (I). In full accord with the views of K. I. Ivanov [25] and the experimental data obtained by us, the scheme of the successive transformations suffered by the formed p-cymene hydroperoxide can be represented as follows:

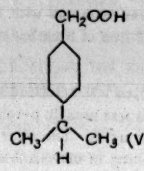


From the presented scheme it can be seen that the main direction of peroxide decomposition under the studied conditions is intramolecular decomposition with the formation of p-tolyl methyl ketone (II), which undergoes further oxidation to the acids (III and IV) or condensation into tarry products.

The second direction, leading to the formation of p-cresol (V) and acetone (VI), is secondary and proceeds insignificantly. The hydroperoxide structure (VII) is apparently responsible for cumic acid formation. Statements exist in the literature [22, 23, 26, 27] on the predominant reaction of the p-cymene methyl group with oxygen at temperatures up to 110°, which, apparently, is associated with the steric hindrance factor (the difficulty of oxygen entrance to the α-carbon atom of the isopropyl group).

It is quite probable that at elevated temperatures the C–C bond of the isopropyl group becomes more labile and the influence of the steric factor vanishes, as a result of which the oxidation proceeds mainly at the α-carbon atom of the isopropyl group, the hydrogen of which appears to be more labile. The above mentioned studies of other

* In percent on the weight of taken p-cymene, based on the metal.



(VII)

investigators [20, 21] also testifies to the high stability of the p-cymene methyl group under the conditions of catalytic liquid phase oxidation at temperatures above 120-140°.

The presented general scheme actually reflects only the decomposition and intramolecular transformations of the peroxide without taking into consideration the reaction of the peroxide decomposition products with hydrocarbons and oxygen. The latter type of peroxide reaction, in accord with the N. N. Semenov theory of chain processes, is the determinant for the quantitative accumulation of intermediate and end oxidation products, and also in the formation of certain secondary reaction products and, in particular, of dicymyl.

The formation of the last can be depicted by the following chain reactions of general form:

$$ROOH \rightarrow RO\cdot + HO\cdot;$$
$$RO\cdot + RH \rightarrow ROH + R\cdot;$$
$$HO\cdot + RH \rightarrow H_2O + R\cdot;$$
$$R\cdot + R\cdot \rightarrow R-R;$$
$$R\cdot + RH \rightarrow R-R + H\cdot.$$

From the presented scheme it follows that the reaction of the free radicals, formed in the decomposition of the hydroperoxide, should lead to the creation of active radicals, which, in the absence of sufficient oxygen, can undergo dimerization on solid surfaces.

Actually, in Experiments 1-7 (see Table), run in the presence of soluble catalysts, only a small amount of dicymyl was formed, on manganese dioxide, or in the presence of well developed solid surfaces, the yield of dicymyl reached 5.4-8.5% (Experiments 10 and 11), which represents 20-31.5% on reacted p-cymene.

However, it should be mentioned that the dimerization of p-cymene proceeds only in the presence of molecular oxygen. It was shown by special experiments that p-cymene, even in the presence of a well developed surface (spun glass), remained practically unchanged under the conditions of prolonged boiling (up to 48 hours) in the absence of oxygen. This indicates that the given reaction should be regarded as one of oxidative dehydrocondensation.

As was to be expected, on increasing the oxygen passage rate, the yield of dicymyl decreases, being the result of the free cymyl radicals reacting with molecular oxygen in accord with the scheme:

$$R\cdot + O_2 \rightarrow ROO\cdot;$$
$$ROO\cdot + RH \rightarrow ROOH + R\cdot, \text{ etc.}$$

The above is fairly conclusive evidence of the fact that the contemporary representations as to the general reaction mechanism for the autooxidation of alkylbenzenes can be extensively used in interpreting the mechanism for the liquid phase catalytic oxidation of p-cymene. In addition, the obtained results show that the mechanisms of the processes for the liquid phase and vapor phase catalytic oxidation of p-cymene have considerable in common [28].

EXPERIMENTAL

The p-cymene used here was isolated from technical sulfite oil by steam distillation after neutralization of the oil with calcium oxide. After drying with calcium chloride and distillation from metallic sodium, the isolated p-cymene had b.p. 171-172° (at 680 mm), d_4^{20} 0.857, n_D^{20} 1.4898.

p-Toluic and terephthalic acids, used for catalyst preparation, were obtained by the catalytic oxidation of p-cymene in the vapor phase [28]. p-Toluic acid had m.p. 179° and neutralization equivalent 136; terephthalic acid had neutralization equivalent 83; its dimethyl ester melted at 138°.

The manganese toluate was prepared by first adding the calculated amount of 0.1 N sodium hydroxide solution to a solution of 6 g of p-toluic acid in 50 ml of water, and then 5.4 g of manganese acetate (c.p.a.). The precipitate was filtered, washed with cold water and dried at 40°. The cobalt and copper toluates were prepared in similar manner, and also manganese terephthalate. Manganese naphthenate was prepared from technical naphthenic acids and manganese chloride by the described method of V. K. Tsyskovsky [6].

The p-cymene was oxidized in a 150 ml three-necked round-bottomed flask, fitted with reflux condenser, oxygen sparger and thermometer. The vapors of the low-boiling products, not condensing in the condenser, were trapped in an ice-cooled Dean-Stark trap. For each experiment 50 g of p-cymene was taken. The reaction temperature was maintained at 170-172°. At the end of experiment the reaction mixture was extracted with 10% sodium bicarbonate solution to remove the acids. The remaining neutral portion was washed free of bicarbonate traces with water and dried over fused sodium sulfate.

The alkaline extract was boiled with activated charcoal. The still warm solution was acidified with hydrochloric acid. The obtained precipitate was filtered, dried at 60°, and weighed. This was usually p-toluic acid. In some experiments it was contaminated with small amounts of terephthalic and cumic acids. The mixed acids were separated by Soxhlet extraction with hot benzene [31]. The terephthalic acid remaining in the thimble distilled above 325°. Its neutralization equivalent was 83; the dimethyl ester melted at 138°. Evaporation of most of the benzene from the benzene extract gave crystals of p-toluic acid with m.p. 178-179°; neutralization equivalent 135-136.

The cumic acid was found in the filtrate after separating the mixed terephthalic and p-toluic acids from the acidified solution. After ether extraction and recrystallization from alcohol, the cumic acid had m.p. 112-114°; neutralization equivalent 163. Its mixture with pure cumic acid melted at 114°.

The neutral portion of the reaction mixture, remaining after removal of the acids with bicarbonate solution, was dried and distilled at 7 mm. Two fractions were collected and analyzed: with b.p. 48-53 and 90-95°. From the catalyzate in some of the experiments we were able to collect a third fraction with b.p. 110-125° (at 7 mm).

The 1st fraction (unreacted p-cymene) had constants close to those of the original products: d_4^{20} 0.858-0.859, n_D^{20} 1.4900-1.4908.

The 2nd fraction had d_4^{20} 0.980-0.987, n_D^{20} 1.5218-1.5230, which corresponds to p-tolyl methyl ketone. It was identified by the melting points of its semicarbazone (202°) and 2,4-dinitrophenylhydrazone (246°). Their mixed melting points with the corresponding derivatives of p-tolyl methyl ketone, prepared by the Friedel-Crafts reaction [29], failed to be depressed. Also, the obtained p-tolyl methyl ketone was oxidized with potassium permanganate to terephthalic acid (81.3% yield) and with calcium hypochlorite to p-toluic acid (75.3% yield).

The 3rd fraction had m.p. 156-156.5° (from benzene). From its melting point, the product corresponds to 1,1,2,2-tetramethyl-1,2-di-p-tolylethane (dicymyl) [32], and not di-p-cymylethane [30].

Found %: C 90.41; H 9.88. M 257 (in benzene). $C_{20}H_{26}$. Calculated %: C 90.16; H 9.84; M 266.

After distillation of the neutral portion, the tarry residue was carefully washed with water and dried to constant weight.

Found %: C 82.98, 83.01; H 7.53, 7.41. M 324 (in benzene).

In the original reaction mixture, in addition to the above indicated products, the qualitative presence of peroxides (by the Ivanov reaction [25]) and of p-cresol (by the Deniges reaction) was shown.

The trap used for trapping the low-boiling products was shown to contain an appreciable amount of acetone (by the iodoform reaction).

SUMMARY

1. The liquid phase oxidation of p-cymene with oxygen in the presence of manganese, cobalt and copper toluates, manganese dioxide, manganese terephthalate, manganese naphthenate and spun glass was studied.

2. A probable reaction mechanism scheme for the catalytic oxidation of p-cymene in the liquid phase was proposed, which scheme is based on the peroxide theory of A. N. Bakh and the chain process theory of N. N. Semenov

3. It was established that under the studied conditions, together with p-cymene oxidation, there occurs its oxidative dehydrocondensation into 1,1,2,2-tetramethyl-1,2,-di-p-tolylethane. The mechanism and conditions for this reaction to be predominant are considered.

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SYNTHESES OF MAGNOLINE ALKALOIDS

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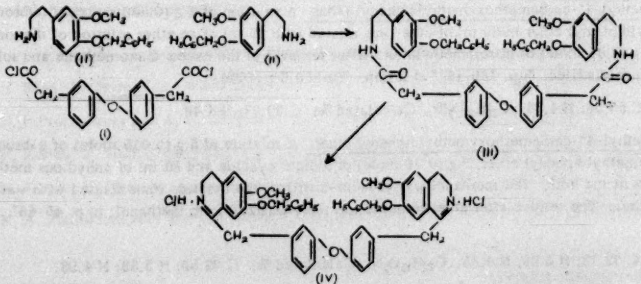
In the tetrahydroisoquinoline group of alkaloids, the so-called biscoclaurine alkaloids occupy a prominent position, for which the presence of two benzyltetrahydroisoquinoline radicals is characteristic, linked through the ether linkage. To this group also belong such alkaloids as d-tubocurarine chloride [1] and magnoline [2]. Up to now the numerous attempts made to synthesize (esterlike) bisbenzyltetrahydroisoquinolines have completely failed to achieve the desired goal.

In 1935, the compound bis(3,4-dimethoxyphenylethylamido)-2'-methoxy-5',4"-dicarboxymethyldiphenyl ether was isolated, being an intermediate in the synthesis of the methyl ether of the biscoclaurine alkaloid dauricine [3]. Recently, studies directed toward the synthesis of cepharanthine have been made [4]. However, in these investigations the structure of the obtained substance was not established exactly, since, of the two possible isomers, only one was isolated. Proceeding from bis(3,4-methylenedihydroxyphenylethylamido)-3',4"-dicarboxymethyldiphenyl ether also gave the bis(dihydroisoquinoline) derivative, for which the melting points of the picrate, styphnate and methiodide were indicated. The synthesis methods used for the base itself, or its intermediates, were not described.

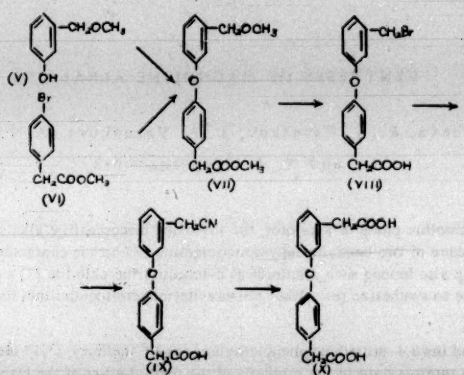
In 1953 [5] the preparation of the quaternary salt with a structure corresponding to that of the methyl ether of opened curarine was realized, which uncovers a method for the synthesis of the alkaloid itself.

We realized the synthesis of 3',4"-{bis[1-(6-methoxy-7-benzyloxy)-3,4-dihydroisoquinolyl]} dimethyldiphenyl ether (IV). The synthesis is of interest as a method for building molecules of this group of alkaloids, since the hydrogenation of the quaternary salt of the obtained compound leads to a substance that differs in its chemical structure from that of the alkaloid magnoline only in the absence of the hydroxy group in the benzene ring of the diphenyl ether (I) (if spatial isomerism is not taken into consideration here).

We realized the synthesis of 3',4"-{bis[1-(6-methoxy-7-benzyloxy)-3,4-dihydroisoquinolyl]} dimethyldiphenyl ether (IV) by the method of simultaneous closure of the two isoquinoline rings of bis[β-(3-methoxy-4-benzyloxy)phenylethylamido]-3',4"-dicarboxymethyldiphenyl ether (III). The latter is obtained by the reaction of the bis-(acid chloride) of 3,4'-dicarboxymethyldiphenyl ether (I) with β-(3-methoxy-4-benzyloxy)phenylethylamine (II).



The 3,4'-dicarboxymethyldiphenyl ether bis(acid chloride) (I) was synthesized by the following sequence of reactions:



The starting compound is 3-methoxymethyl-4'carbomethoxymethyldiphenyl ether (VII), which is obtained by the reaction of 3-hydroxybenzyl alcohol methyl ether (V) with the methyl ester (VI) of p-bromophenylacetic acid in the presence of copper powder. By reaction with hydrobromic acid in glacial acetic acid, the 3-methoxymethyl-4'-carbomethoxymethyldiphenyl ether is transformed into 3-bromo-4'-carboxymethyldiphenyl ether (VIII). The latter, when heated with alcoholic sodium cyanide solution, forms 3-cyanonmethyl-4'-carboxymethyldiphenyl ether (IX). The saponification of the nitrile group with an aqueous-alcohol solution of potassium hydroxide leads to 3,4'-dicarboxymethyldiphenyl ether (X). By heating with thionyl chloride, the obtained dicarboxylic acid is converted into the bis(acid chloride) (I), which, with the hydrochloride of (3-methoxy-4-benzyloxy)phenylethylamine (II), gives bis[β-(3-methoxy-4-benzyloxy)phenylethylamido]-3',4'-dicarboxymethyldiphenyl ether (III). The closure of the isoquinoline rings leads to the dihydrochloride of 3',4"-{bis[1-(6-methoxy-7-benzyloxy)-3,4-dihydroisoquinolyl]}-dimethyldiphenyl ether (IV).

EXPERIMENTAL

3-Bromomethyl-4'-carboxymethyldiphenyl Ether (VIII). A solution of 4.3 g (0.015 mole) of 3-methoxymethyl-4'-carbomethoxymethyldiphenyl ether in 95 ml of glacial acetic acid, containing 25% of hydrogen bromide, was allowed to stand for 3 days. The solution was poured into 600 ml of water and the obtained precipitate was filtered. Yield 4.33 g (90%). After recrystallization from ethyl alcohol, m.p. 107-109°.

Found %: C 55.78; H 3.96. $C_{15}H_{13}O_3Br$. Calculated %: C 56.07; H 4.05.

3-Bromomethyl-4'-carbomethoxymethyldiphenyl Ether. A solution of 1 g (0.003 mole) of 3-bromomethyl-4'-carboxymethyldiphenyl ether in 30 ml of ether was treated with 10 ml of an ether solution of diazomethane, prepared from 1 g (0.01 mole) of nitrosomethylurea. After removal of the excess diazomethane and solvent, the residue was vacuum-distilled. B.p. 189-190° at 2 mm. Yield 0.6 g (60%).

Found %: C 57.58; H 4.88. $C_{16}H_{15}O_3Br$. Calculated %: C 57.31; H 4.48.

3-Cyanomethyl-4'-carbomethoxymethyldiphenyl Ether. A mixture of 5 g (0.015 mole) of 3-bromomethyl-4'-carbomethoxymethyldiphenyl ether, 3 g (0.06 mole) of sodium cyanide and 80 ml of anhydrous methanol was heated for 2 hours at the boil. The methanol was vacuum-distilled, the reaction mass diluted with water, and then extracted with ether. The residue after ether removal was recrystallized from methanol, m.p. 45-46°. Yield 2.95 g (70%).

Found %: C 72.73; H 5.29; N 4.89. $C_{17}H_{15}O_3N$. Calculated %: C 72.59; H 5.33; N 4.98.

3-Cyanomethyl-4'-carboxymethyldiphenyl Ether (IX). A mixture of 3.21 g (0.01 mole) of 3-bromomethyl-4'-carboxymethyldiphenyl ether, 2.5 g (0.05 mole) of sodium cyanide and 125 ml of anhydrous methanol was heated for 1.5 hours at the boil. The methanol was vacuum-distilled, the residue dissolved in water, filtered, acidified with sulfuric acid and then extracted with ether. The residue after ether removal gradually solidified. After recrystallization from carbon tetrachloride, m.p. 74-76°. Yield 2.15 g (73%).

Found %: C 71.75; H 4.65; N 5.23. $C_{16}H_{13}O_3N$. Calculated %: C 71.9; H 4.87; N 5.24.

3,4'-Dicarboxymethyldiphenyl Ether (X). A solution of 2.4 g (0.009 mole) of 3-cyanomethyl-4'-carboxymethyldiphenyl ether in 3.5 ml of alcohol was treated with 1.44 g (0.036 mole) of sodium hydroxide in 2.5 ml of water. The reaction mass was heated at the boil for 10 hours, extracted with ether to remove impurities, the aqueous solution acidified with dilute hydrochloric acid, and the obtained precipitate of dicarboxylic acid filtered. After reprecipitation and recrystallization from water, m.p. 162-164°. Yield 1.8 g (72%).

Found %: C 67.52, 67.53; H 4.88, 5.09. $C_{16}H_{14}O_5$. Calculated %: C 67.14; H 4.90.

Bis[β-(3-methoxy-4-benzyloxy)phenylethylamido]-3',4"-dicarboxymethydiphenyl Ether (III). A mixture of 4 ml (0.056 mole) of freshly distilled thionyl chloride and 1.43 g (0.005 mole) of 3,4'-dicarboxymethyldiphenyl ether was heated for 2 hours on the boiling water bath. The excess thionyl chloride was vacuum-distilled and its last traces removed by the repeated addition of dry benzene. Each time the benzene was distilled off, after which the residual bis(acid chloride) was dissolved in 10 ml of chloroform. At the same time, a suspension of 2.92 g (0.01 mole) of the hydrochloride of 3-methoxy-4-benzyloxyphenylethylamine [5] in 30 ml of chloroform was prepared and with stirring 15 ml of a 5 % potassium hydroxide solution (0.13 mole) was added. Then over 40 minutes was gradually added the obtained, as indicated above, solution of 3,4'-dicarboxymethyldiphenyl ether bis(acid chloride) and about 18 ml of 5% potassium hydroxide solution. The reaction was kept slightly alkaline. After 15 minutes the chloroform layer was separated, washed with dilute hydrochloric acid, water, and dried. After removal of the solvent, there remained a gradually congealing oily residue. When rubbed with ether it gives a nearly colorless powder. After recrystallization from ethyl alcohol, m.p. 125-126°. Yield 2.5 g (65.4%).

Found %: C 75.27; H 6.55; N 3.82. $C_{48}H_{48}O_7N_2$. Calculated %: C 75.39; H 6.28; N 3.66.

3',4"-{Bis[1-(6-methoxy-7-benzyloxy)-3,4-dihydroisoquinolyl]}-dimethyldiphenyl Ether (IV). To a stirred suspension of 1.15 g (0.0015 mole) of bis[β-(3-methoxy-4-benzyloxy)phenylethylamido]-3',4"-dicarboxymethyldiphenyl ether in 12 ml of dry toluene was added 3 ml of freshly distilled phosphorus oxychloride. The reaction mass was heated at the boil for 1.5 hours, then the toluene and excess phosphorus oxychloride were distilled in vacuo, while the residue was dissolved in alcohol. The addition of ether gave the dihydrochloride of 3',4"-{bis[1-(6-methoxy-7-benzyloxy)-3,4-dihydroisoquinolyl]}-dimethyldiphenyl ether. After recrystallization from ethyl alcohol, m.p. 139-142°.

Found %: N 3.66, 3.35. $C_{48}H_{46}O_5N_2Cl_2$. Calculated %: N 3.49.

The picrate was obtained by reacting alcohol solutions of the dihydrochloride of the base and picric acid. After two recrystallizations from ethyl alcohol, m.p. 206-207°.

Found %: C 60.84; 60.68; H 4.37, 3.98; N 9.23, 9.42. $C_{60}H_{50}O_{19}N_8$. Calculated %: C 60.66; H 4.21; N 9.43.

SUMMARY

Thy synthesis of 3',4"-{bis[1-(6-methoxy-7-benzyloxy)-3,4-dihydroisoquinolyl]}-dimethyldiphenyl ether was accomplished through a number of steps.

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SOME PROPERTIES OF 17β-HYDROXYSTEROID p-TOLUENESULFONIC ACID ESTERS

III. REACTION OF Δ^5-ANDROSTEN-3β,17β-DIOL 17-TOSYLATE AND ITS 3-ACETATE WITH ORGANOMAGNESIUM COMPOUNDS AND WITH MAGNESIUM HALIDES

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Earlier it was shown [1] that the 17-tosyl esters of hydroxysteroids are incapable of exchange decomposition reactions even when heated up to 100°; at more elevated temperature the main reaction is cleavage of p-toluenesulfonic acid, accompanied by pinacolin rearrangement. The reactions of the tosylates of steroids with Grignard reagent are not described in the literature.

We reacted Δ^5-androsten-3β,17β-diol 17-tosylate (I) with methylmagnesium iodide in ether and readily obtained 17-iodo-Δ^5-3-androstenol (II). However, with ethylmagnesium chloride under the same conditions, the original substance (I) was recovered unchanged. At higher temperature (60-65°) in ether-benzene mixture a tarry deposit was obtained, which gave a positive Kagi-Miescher reaction [2], characteristic for retrosteroids that are formed as the result of cleavage of the tosyl residue at C_{17}. After acetylation, the tarry residue was chromatographed in gasoline solution on aluminum oxide. The crystals isolated from the gasoline eluates, recrystallized once from alcohol, had m.p. 95-96°. The mixed melting point with the retroandrostadienol 3-acetate (III) (m.p. 94-96°) failed to be depressed.

The substance (III) had been isolated by us earlier [1] from a mixture of retro compounds, obtained by boiling Δ^5-androsten-3β,17β-diol 3-acetate, 17-tosylate (IV) in acetic acid in the presence of potassium or silver acetate; for its purification the compound had to be recrystallized 12 times from alcohol. It contained a ditertiary double bond, as was shown by preparing from it a crystalline, azure nitrosochloride.

As a result, the reaction of the 17-tosyl ester of Δ^5-androsten-3β,17β-diol with alkylmagnesium halides proceeds smoothly in ether in the case of methylmagnesium iodide with replacement of the tosyl group by halogen; at higher temperature hydrogen halide acid is cleaved, accompanied by retropinacolin rearrangement with the formation of a homogeneous retroandrostadienol. A similar reaction is also found in the terpene series in the transformation of bornyl tosylate into camphene via the Grignard reaction [3].

We also studied the reaction of steroid 17β-tosyl esters with the halides of sodium, lithium, zinc and magnesium.

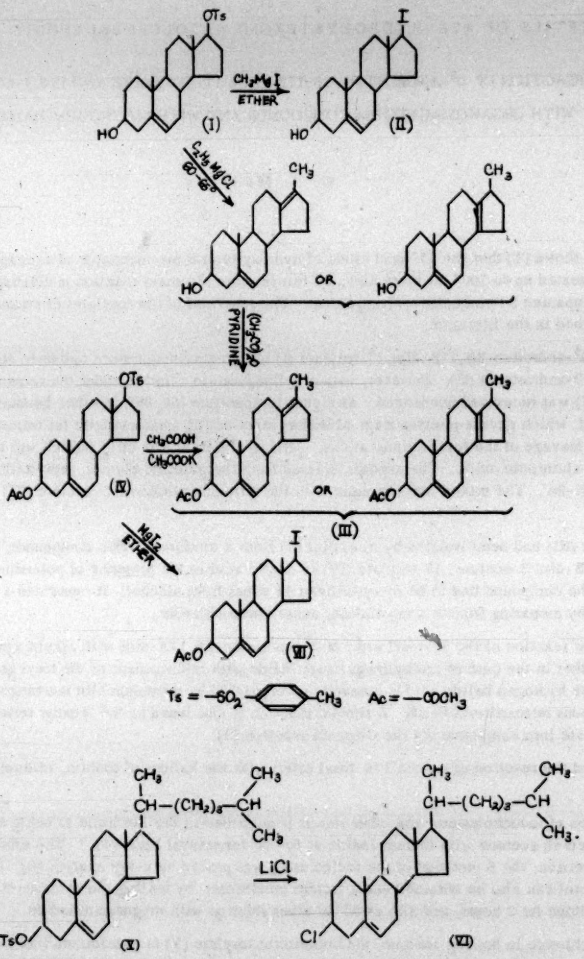
The preparation of iodocholesterol and other sterols is described in the literature as being effected by the heating of their tosyl esters in acetone with sodium iodide at 60-70° for several hours [4]. * The substitution reaction proceeds without inversion; the β-position of the iodine at C_3 was proved by x-ray analysis [5]. It was shown by us that the iodocholesterol can also be obtained under milder conditions: by boiling the cholesterol tosylate with sodium iodide in acetone for 2 hours, and also at 35° in ether solution with magnesium iodide.

With lithium chloride in boiling acetone, the cholesterol tosylate (V) is transformed into the chlorocholesterol (VI), identical with the β-chlorocholesterol that is obtained by the reaction of cholesterol with thionyl chloride in pyridine [6].

Attempts to prepare the 17-halo derivative from (IV) by the method of prolonged heating in a sealed tube on the boiling water bath with sodium iodide in acetone, with lithium chloride in methanol, with zinc iodide in ether and with magnesium iodide in acetone at 45° led in all cases to recovery of the original unchanged Δ^5-androsten-3β-17β-diol 3-acetate, 17-tosylate. Replacement of the 17-tosyl group in compound (IV) by iodine under the conditions of heating with magnesium iodide in ether solution at 35° for 2 hours was completely unexpected, which

* See [3].

replacement gave 17-iodo-Δ^5-3β-androstenol 3-acetate (VII). This reaction begins even at room temperature, since immediately after adding the magnesium iodide in ether solution there is observed the separation of magnesium p-toluenesulfonate. Apparently, the magnesium iodide etherate is capable of replacing the 17-tosyl group of steroids by iodine.



It is known that the alicyclic esters of arylsulfonic acids when heated with sodium iodide in acetone solution [3] practically fail to form halo derivatives, while at 100° they give unsaturated compounds. We reacted bornyl tosylate with magnesium iodide in ether; the separation of the magnesium p-toluenesulfonate also began here even at room temperature. Boiling for 2 hours led to complete disappearance of the tosyl group in the borneol (absence of reaction for sulfur). The reaction product, obtained after washing the colorless ether extract with sodium sulfite and water, gave an intense reaction for halogen; due to its unstable nature, we were unable to isolate the iodoborneol in pure form.

The ease with which the 17-iodo derivative is formed when Δ^5-androsten-3β,17β-diol 3-acetate, 17-tosylate is reacted with magnesium iodide in ether solution gives basis to assume that also in the reactions with alkylmagnesium iodides the replacement of the 17-tosyl group by iodine will proceed as the result of the magnesium iodide, found present in the Grignard reagent equilibrium system:

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \text{ [7].}$$

EXPERIMENTAL

17-Iodo-Δ^5-3β-androstenol (II). To a solution of methylmagnesium iodide, prepared from 0.15 g of magnesium and 0.5 g of methyl iodide in 20 ml of anhydrous ether, was added in drops with vigorous stirring and ice water cooling a solution of 0.96 g of Δ^5-androsten-3β,17β-diol 17-tosylate in 30 ml of ether; a white spongy precipitate was formed immediately. Then the reaction mass was boiled for 3 hours. After decomposition with water, the mixture was acidified with 3% sulfuric acid. The ether solution was washed free of iodine traces with sodium bisulfite solution and water until the tests with silver nitrate and barium chloride were negative; the ether solution was then dried over sodium sulfate. Removal of the solvent by distillation gave 0.6 g of crystalline precipitate, which was recrystallized from methanol. Needles with m.p. 135-135.5°, slightly soluble in alcohol and acetone.

Found %: C 56.68; H 7.24. $C_{19}H_{29}OI$. Calculated %: C 56.97; H 7.31.

Reaction of Δ^5-Androsten-3β-17β-diol 17-Tosylate with Ethylmagnesium Chloride. A solution of 0.7 g of the 17-tosylate in 30 ml of anhydrous ether was gradually added to 10 ml of an ether solution of ethylmagnesium chloride, prepared from 0.12 g of Mg and ethyl chloride. From the reaction mass was distilled 20 ml of ether, then 25 ml of anhydrous benzene was added and the reaction mixture heated for 4 hours at a bath temperature of 55-60°. The remainder of the treatment was the same as in the previous experiment. After distilling off the solvent, the tarry residue gave a positive Kagi-Miescher reaction; we were unable to isolate a crystalline product from it. For acetylation, 0.55 g of the tarry residue was dissolved in 2.5 ml of anhydrous pyridine, 0.6 g of acetic anhydride was added and the whole allowed to stand overnight. Then the reaction mass was poured into water, acidified with 3% hydrochloric acid, stirred for 1.5 hours, and extracted with ether. The ether extract was freed of pyridine by washing with 2% hydrochloric acid solution, then with water, and finally it was dried over sodium sulfate. Removal of the solvent by distillation gave 0.52 g of tarry residue, which crystallized when gasoline was added, after which the precipitate was filtered and washed with ether. The yield of substance with m.p. 160-161° was 0.2 g; its mixture with (IV) failed to depress the melting point. The substance, soluble in the gasoline, was chromatographed on aluminum oxide. Elution first with gasoline, and then with a 1:1 gasoline-benzene mixture, gave a colorless oil showing incipient crystallization; when alcohol was added a precipitate with m.p. 93-93.5° separated; one recrystallization from alcohol gave colorless hexagonal plates of the retroandrostadienol 3-acetate (III) with m.p. 95-95.5°.

Found %: C 80.16; H 9.60. $C_{21}H_{30}O_2$. Calculated %: C 80.21; H 9.62.

Reaction of Δ^5-Androsten-3β,17β-diol 3-acetate, 17-tosylate with Magnesium Iodide in Ether. To a solution of magnesium iodide, prepared from 0.35 g of iodine and 0.033 g of magnesium in 20 ml of anhydrous ether, was gradually added a solution of 0.15 g of Δ^5-androsten-3β,17β-diol 3 acetate, 17-tosylate in 20 ml of anhydrous ether and the mixture boiled for 2 hours; immediately a yellowish-white precipitate of magnesium p-toluenesulfonate separated. The reaction mass was poured into water and the ether layer was washed with water; the ether extract was dried over sodium sulfate. Removal of the ether by distillation gave 0.14 g of tarry residue. Trituration with alcohol gave a crystalline precipitate with m.p. 145-147°; after recrystallization from alcohol with charcoal, m.p. 151-152°.

Found %: C 56.83; H 7.03; I 28.40. $C_{21}H_{31}O_2I$. Calculated %: C 56.99; H 7.06; I 28.70.

Cholesterol Tosylate (V) [8]. To a solution of 2 g of cholesterol (m.p. 147°) in 4 ml of dry pyridine was gradually added with ice cooling 2.1 g of p-toluenesulfonyl chloride and the mixture let stand at room temperature for 20 hours. The cholesterol tosylate with m.p. 131° was obtained. Yield 82%.

Reaction of Cholesterol Tosylate with Lithium Chloride in Acetone. Preparation of Chlorocholesterol (VI). A mixture of 0.1 g of cholesterol tosylate and 0.1 g of anhydrous lithium chloride in 10 ml of dry acetone was heated for 9 hours in a sealed tube at 92-94°. The acetone was distilled in vacuo to dryness, the precipitate was dissolved in ether, then washed with water until a negative test for halogen was obtained with $AgNO_3$, after which the ether extract was dried over sodium sulfate. The solvent was removed by distillation to give a crystalline precipitate with m.p. 91-92°; after recrystallization from acetone, m.p. 95°; its mixed melting point with the β-chlorocholesterol obtained from cholesterol and thionyl chloride [6] failed to be depressed.

Bornyl Tosylate. To 0.7 g of borneol in 4 ml of pyridine at 0° was added 0.95 g of p-toluenesulfonyl chloride [6] and the whole allowed to stand until the next day at room temperature. The reaction mass was dissolved in chloroform, the chloroform solution washed with 2% hydrochloric acid solution, then water, and finally dried over sodium sulfate. Removal of the chloroform by distillation gave a tarry residue which crystallized after ether was added at −8°. The precipitate was filtered and washed with ether. M.p. 66-67°, as described in the literature [9].

Reaction of Bornyl Tosylate with Magnesium Iodide in Ether. A colorless magnesium iodide solution, prepared from 0.032 g of magnesium and 0.32 g of iodine in 7 ml of anhydrous ether, was added to a solution of 0.2 g of bornyltosylate in 2 ml of anhydrous ether; here a precipitate of magnesium p-toluenesulfonate began to separate immediately. After boiling for 3 hours, the mixture was poured into water, the ether layer washed with water, then with sodium sulfate solution, and again with water (tested with $AgNO_3$). The completely colorless ether solution gave a strong reaction for halogen. The ether extract was dried over sodium sulfate. The ether was distilled in vacuo. Already on standing and during distillation the ether solution turned yellow. The obtained tarry brown precipitate was shown to contain free iodine and gave a negative test for sulfur.

SUMMARY

1. It was shown that Δ^5-androsten-3β,17β-diol 17-tosylate reacts with methylmagnesium iodide in ether medium to give 17-iodo-Δ^5-3β-androstenol, while with ethylmagnesium chloride at 60° there occurs cleavage of p-toluenesulfonic acid and the 3-retroandrostadienol is obtained.

2. It was shown that the tosyloxy group in Δ^5-androsten-3β,17β-diol 17-tosylate can be replaced by iodine only under the influence of magnesium iodide in ether solution. The reaction fails to proceed in the presence of zinc iodide in ether solution, or in the presence of magnesium iodide or of the iodides of the alkali metals in acetone solution.

3. A convenient method for the preparation of the individual 3β-retroandrostadienol and of the 17-iodo derivatives of steroids from the corresponding 17-tosylates was proposed.

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THE CATALYSTS AND MECHANISM OF THE LEUCKART REACTION

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It was shown by one of us [1] that the Leuckart reaction is accelerated in the presence of hydrogenation catalysts (nickel, cobalt, platinum, palladium); statements exist on the effectiveness of adding water-removing media [2] or acidic agents: formic and acetic acids and the chlorides of magnesium, zinc, iron and cobalt [3, 4]. However, Alexander and Wildmann [5] assert that water-removing media hinder the reaction, while acidic agents fail to show a positive influence.

We studied the influence of additions on the rate and direction of the reaction between cyclohexanone and formamide. It was revealed that skeletal nickel is a more active catalyst than the nickel-nickel oxide mixture obtained in the decomposition of the formate. With skeletal nickel the evolution of CO_2, indicating the beginning of reaction, proceeds at 30-35°, with nickel from the formate at 110°, and without catalyst – at 150-160°. The unleached alloy of nickel with aluminum is less active than the skeletal nickel. The cobalt catalyst (from the formate) is weaker than the corresponding nickel catalyst, while colloidal iron is even weaker. The acid aluminosilicate dehydration catalyst gave good results.

Usually an excess of formamide is used in the Leuckart reaction, at times up to 18 moles [5]. We used 4 moles of formamide for 1 mole of the ketone (an increase to 6 moles failed to raise the yield). The reaction proceeds slowly with pure formamide and requires strong heating (the reaction is not complete after 6 hours at 130-140°); consequently, we used a mixture of formamide with ammonium formate (12-15%) or formic acid (8%). Hydrogen chloride is a vigorous catalyst for the reaction (the reaction is complete after 40-50 minutes at 130°). The best results (98% yield) were obtained with skeletal nickel and an excess of formic acid (Table 1). With pure formamide the catalyst fails to essentially influence the reaction course. As a result, our experiments support the fact that the reaction is accelerated by substances that facilitate dehydration or hydrogenation, and also by acidic agents.

The yields in this reaction depend on the method of treating the reaction mixture and, for example, in the hydrolysis with concentrated alkali, can drop to zero [6]. According to our data, the hydrolysis with hydrochloric acid proceeds well if the formed formic acid is permitted to escape by evaporation. The hydrolysis proceeds more rapidly in the presence of nickel, but the isolation of the substance is made difficult by the presence of nickel salt.

The low yields obtained in acid hydrolysis are determined by the difficulty of extracting the substance from the large mass of salts. The hydrolysis is complete in 2 hours when the reaction mixture is boiled with dilute alkali, but repeated extraction of the base is required. When the reaction mass is treated with concentrated sodium hydroxide solution (better if heated), a precipitate of the sodium-enolate of formylcyclohexylamine is obtained, which permits easy isolation of the reaction products. Formyldicyclohexylamine is hydrolyzed almost instantaneously in alkaline medium, in which connection the base is adsorbed by the enolate precipitate and is then easily removed by washing with ether. When the enolate is heated with water for a short time, the formylcyclohexylamine separates as a layer. Prior to the treatment with alkali it is only necessary to remove traces of the catalyst. The use of potassium hydroxide is less convenient, since the potassium-enolate is more soluble (a greater excess of alkali is required).

The proportion of primary and secondary amines depends on the order of reagent mixing and the acidity of the medium. The yield of the primary amine is increased if the ketone is introduced into heated formamide. If formamide and formic acid are added to an excess of ketone then the secondary amine is preferentially formed, but part of the ketone is recovered unchanged. The additions of nickel preferentially increase the yield of secondary amine due to augmented decomposition of the formic acid and reduction in the acidity of the medium. In alkaline medium, i.e., with additions of pyridine, ammonia, sodium formate or urea, the reaction proceeds very vigorously (especially in the presence of nickel), giving chiefly dicyclohexylamine (Table 2). On the other hand the introduction of excess acid can practically exclude the formation of the secondary amine.

The obtained results, in addition to preparative interest, permit making certain conclusions as to the reaction mechanism. Many authors postulate that the free amine is formed in the Leuckart reaction, which is then formylated [2, 6, 7]. According to our data, under the conditions of the reaction, the formamide acylates the cyclohexylamine to the extent of only 32%. Hydroamination in acetic anhydride gives the formyl derivative (yield 75.9%), but not the

TABLE 1

Influence of Reaction Conditions on the Yield of Cyclohexylamine (0.3 Mole of Cyclohexanone + 1.2 Moles of Formamide-Formate Mixture)

Method of Reagent Introduction	Temperature	Total Heating Time (in hours)	Catalyst	Separation Method	Yield (in %)				Amount of tar (in g)
					RNH_2	RNHCHO	R_2NH	Total	
Ketone to the formamide (over 0.5 hour)	130°	1.0	Skeletal Ni	Through the potassium-enolate	10.4	43.1	38.6	92.1	1.2
"	110-130°	1.0	"	Hydrolysis with 2N NaOH (2 hours)	41.2	–	41.8	83.0	3.2
"	140	1.0	"	By leaching	–	65	27	92	–
Ketone to the formamide + 1 mole of HCOOH (over 1.5 hours)	120-130	3.0	"	"	–	98.0	–	98.0	–
The whole was mixed at one time	80	8.0	"	Through the sodium-enolate	3.8	30.0	59.3	93.1	1.4
	120-140	1.5							
"	140	1.0	"	"	–	69.0	23.6	92.6	1.8
"	130	1.5	"	Hydrolysis with 2N NaOH (2 hours)	40.8	–	42.0	82.8	–
"	125	1.0	"	Hydrolysis with Conc. HCl (2 hours)	16.4 • (+ 40.0)	5.5	29.6	91.5	–
"	125	1.5	Alumino-silicate	By leaching	–	36.2	43.8	80.0	–
"	125	1.5	Co/CoO	"	–	42.0	36.9	78.9	–

• Steam distillation of the alkaline mass, remaining after 20 extractions with ether, gave an additional 40% yield of cyclohexylamine as the hydrochloride.

TABLE 2

Influence of Acidic and Alkaline Agents on the Direction of Reaction between Cyclohexanone and Formamide

(Catalyst – Skeletal Nickel. Amounts Given in Moles Per Mole of Cyclohexanone. Ketone Added to the Heated Formamide)

Amount of $HCONH_2$	Addition		Time of Heating (in Hours)	Temperature	Yield (in %)		
	Formula	Amount			RNH_2	R_2NH	Total
6.0	HCOOH	0.3	1.5	120°	55.2 (a)	26.0	81.2
4.5	HCOOH	2.0	3.0	120-130	98.0	–	98.0
0.5	HCOOH	1.5	3.0	120	14.7	77.8	91.5 (b)
1.6	HCOOH	2.0	4.0	115	85.2 (c)	–	–
	$HCOONH_4$	0.4					
3.2	$(CH_3CO)_2O$	3.2	2.0	120-130	79.9	8.2	88.1
	$HCOONH_4$	0.5					
3.0	NH_3	Excess	2.0	140	28.2	52.6	80.8
	$HCOONH_4$	0.5					
3.0	$C_5H_5N \cdot HCOOH$	0.6	2.5	115	18.0	68.1	86.1
2.6	$HCOONH_4$	0.4	2.0	130 (d)	9.8	74.4	84.2
	HCOONa	1.0					
–	NH_2CONH_2	1.6	3.0	110	9.5	84.8	94.3
	HCOOH	2.0					
–	NH_2CONH_2	1.6	5.0	110-115	86.0	–	–
	HCOOH	10.0					

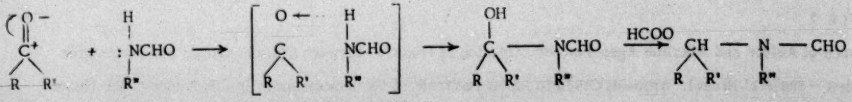
Remarks. a) Free base isolated, b) 42.8% of the ketone reacted (yield based on reacted ketone), c) isolated as the hydrochloride, d) catalyst – Ni – Al catalyst.

acetyl, although acetic anhydride is the stronger acylation agent (when cyclohexylamine is treated with a mixture of formamide and acetic anhydride only the acetyl derivative is obtained). Finally, under mild conditions for the reaction, the free amine in general is not obtained.

If we start from the assumption that the primary process for the reaction is dissociation of the formamide with the formation of ammonia [4, 7, 8], then an excess of the latter should increase the yield of primary amine; however, in this case only the secondary amine and N-formylcyclohexylamine are obtained. In addition, the thermal decomposition of formamide (in the presence of nickel) begins only at 140°, whereas the hydroamination already proceeds at 110°. The cyclohexylformamide begins to decompose only at 190°; consequently, the formation of the dicyclohexylamine would be impossible under our conditions. In acetic anhydride medium the formamide-formate mixture begins to decompose with CO evolution already at room temperature, but even after complete decomposition of the formamide (in a period of 12 days) the ketone fails to react. If such a mixture is heated to 110°, then CO_2 instead of CO is evolved, and the hydroamination proceeds smoothly. As a result, the conditions for the dissociation of formamide do not coincide with the conditions for the Leuckart reaction.

Apparently, the reaction has an ionic character [3-5], in which connection the first step is the addition of the formamide to the carbonium ion. Pollard and Young [9] proposed an ionic scheme for the mechanism of the reaction, formally constructed and based on the resonance theory. Recently, A. I. Titov and A. N. Baryshnikova [10] postulated a different scheme, which assumes the formation of first the primary amine, and then of its already formylated derivative.

We postulate that the first process is the ionic addition of formamide to the ketone. Acidic agents facilitate the formation of the carbonium ion. Only bond polarization takes place in neutral medium, insufficient for rapid progress of the reaction. In alkaline medium there occurs strong polarization of the N–H bond in formamide, which also facilitates addition. The ketone with formamide gives an intermediate compound, which, with the migration of a proton, is transformed into a formylaminocarbinol (substances of this nature were obtained in the reaction of amides with aldehydes [11] or ketones [12]). Then the carbinol is directly reduced by the formate ion through the step of water cleavage [8] or formation of the formate [1, 13]. Hydrogenation catalysts accelerate the decomposition of the formate ion, i.e., they facilitate the reduction.



In the case of dialkylformamides, where there are no hydrogen atoms connected to the nitrogen, the reaction proceeds slowly and only with extremely reactive carbonyl compounds. The mechanism of this reaction (Wallach reaction) should be considered separately.

At the time that this paper was being prepared for publication, we received the paper by Mousseron [14], where similar conclusions were made as to the role of nickel and the influence of acidic additions. Alkaline additions were not studied by Mousseron; his yields of amines failed to exceed 65%. When Mousseron repeated our older work [15], he obtained a different ratio of secondary and tertiary amines for the reaction of methylformamide with cyclopentanone, which is explained by the influence of the aluminosilicate catalyst used by us as ebullition agent. In our case, when the reaction was run for a long time, the formic acid decomposed, the acidity of the medium dropped, and the tertiary amine was predominantly obtained. When the experiment was run with sufficient acidity, the results agreed with those obtained by Mousseron.

EXPERIMENTAL

The formamide-formate mixture was prepared by passing ammonia into 85% formic acid to saturation or by adding ammonium carbonate to cessation of carbon dioxide evolution, after which water was removed by distillation until the temperature of the mixture reached 150°. The residual liquid contains 1 mole of ammonium formate for 6-7 moles of formamide. To obtain the formamide, the heating was continued until the temperature of the mixture reached 175-180°, and then the mixture was vacuum-distilled. Skeletal nickel was obtained by leaching the alloy (containing 40% Al) with 40% sodium hydroxide solution, and after being washed twice with water it was immediately used for reaction.

Formylcyclohexylamine. To 450 g of mixture, containing 6.0 moles of formamide and 2.5 moles of formic acid, was added 1.0 g of skeletal nickel, the whole heated to 120° (thermometer in the mixture) in a Wurtz flask with descending condenser, and in drops over 1.5 hours 150 g (1.4 moles) of cyclohexanone added. Then heating was continued for another 1.5 hours (120-130°), in which connection the small amounts of ketone that steam-distilled were returned to the reaction flask. To the hot mixture was cautiously added 300 ml of 50% sodium hydroxide and the liquid decanted from the resulting precipitate. The precipitate was treated with 100 ml of water, the mixture heated for 1-2 minutes to dissolve the substance and achieve oil separation, and the oil extracted with ether and then distilled. The yield of formylcyclohexylamine was 177 g (98%).

B.p. 153-154° (19 mm), 268-274° (751 mm); m.p. 27°, n_D^{17} 1.4892, d_4^{17} 1.0123, MR_D 35.98; calc. 36.07.

Found %: C 65.40; H 10.46. $C_7H_{13}ON$. Calculated %: C 66.14; H 10.24.

Cyclohexylamine Hydrochloride. To 100 g (~2 moles) of the formamide-formate mixture, 100 g (~2 moles) of 85% formic acid and 0.5 g of skeletal nickel was added in drops under boiling over 1.5 hours 48 g (0.5 mole) of cyclohexanone and the mixture heated another 2.5 hours (temperature of the mixture ~115°). Then the mixture with 500 ml of concentrated hydrochloric acid was evaporated to dryness, the dry residue decomposed with an excess of 50% potassium hydroxide, and the whole boiled under reflux to complete removal of ammonia. The free amine was distilled into hydrochloric acid, the distillate evaporated to dryness, washed with benzene, triturated with ether, dried in a vacuum-desiccator for 5 days over potassium hydroxide, and recrystallized from anhydrous alcohol. The yield of cyclohexylamine hydrochloride was 58.6 g (85.2%), m.p. 207°, which m.p. corresponds to the literature [16].

Dicyclohexylamine. A mixture of 30 g (0.5 mole) of urea, 29.4 g (0.3 mole) of cyclohexanone, 20 g (0.3 mole) of 85% formic acid and 0.5 g of skeletal nickel was prepared. With heating for 3 hours at 110° another 20 g (0.3 mole) of formic acid was added dropwise. After the usual treatment with alkali, there was obtained 3.6 g (9.5%) of formylcyclohexylamine and 23 g (84.8%) of dicyclohexylamine, b.p. 137-139° (19 mm); 248-250° (751 mm); hydrochloride, m.p.335° (from alcohol). Literature: b.p. 115-120° (10 mm); 245-254° (760 mm); hydrochloride, m.p. 337° [17].

Acylation of Cyclohexylamine. To a boiling mixture of 18.5 g (0.45 mole) of formamide, 47.7 g (0.45 mole) of acetic anhydride and 0.5 g of skeletal nickel was added over 20 minutes 9.9 g (0.1 mole) of cyclohexylamine, the whole heated another 40 minutes and then decomposed with 10% sodium hydroxide solution. After cooling the acetylcyclohexylamine was separated and washed with water. Yield 10.9 g (74%), m.p. 102-103°. Literature: m.p. 104° [18]. Formylcyclohexylamine was absent. In a similar experiment (2 hours, 130°) without the acetic anhydride

the yield of formylcyclohexylamine was 32%.

Sodium-Enolate of Formylcyclohexylamine. To a solution of 12.7 g (0.13 mole) of formylcyclohexylamine in 300 ml of anhydrous ether was added 2.37 g (0.15 mole) of finely comminuted sodium. After stirring for 12 hours and distilling off the ether there was obtained 7.5 g of white powder, which suffers hydrolysis under the addition of water or alcohol. M.p. 200° (decompn.). This substance was boiled for 6 hours with 31.2 g (0.2 mole) of ethyl iodide and 100 ml of xylene. After treatment with 150 ml of 10% hydrochloric acid the formyl derivatives were separated and hydrolyzed with 5% sodium hydroxide (boiling for 4 hours). Distillation of the ether extract gave 4.8 g (49.2%) of cyclohexylamine and 2.9 g (22.8%) of ethylcyclohexylamine, b.p. 163-165° (761 mm); picrate, m.p. 132° (from alcohol). Literature: b.p. 164° (760 mm); picrate, m.p. 133° [19].

SUMMARY

1. It was shown that alkaline additions in the presence of skeletal nickel accelerate the Leuckart reaction, in which connection under their influence the secondary amine is predominantly formed.

2. It was found that the Leuckart reaction proceeds through the stage of formamide dissociation. The primary reaction product is not the amine, but instead is its formyl derivative.

3. The reasons for the variable yields under acid and alkaline hydrolysis conditions were elucidated.

4. A convenient method was given for the preparation of cyclohexylamine hydrochloride (yield 85%), formylcyclohexylamine (yield 98%) and dicyclohexylamine (yield 85%).

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LETTER TO THE EDITOR

In No. 4 of the "Journal of General Chemistry" for this year in the paper by A. A. Petrov and V. Lyudvig, entitled "Conjugated Systems. LVII. The Condensation of α-Vinylpyridine with Diene Hydrocarbons", on pages 739 (forth paragraph) and 742 (last paragraph) the proofreader through my fault permitted an absurd error to pass. It is obvious that the compound identified as α-(o-tolyl)pyridine is not the condensation product of piperylene with α-vinylpyridine, as described in the paper, but instead is the substance obtained in the dehydrogenation of the latter over palladium. For identification purposes the α-(o-tolyl)pyridine was prepared by the reaction of o-tolyl-lithium with pyridine. The method (from pyridyllithium) indicated in the paper gives poor results. The question as to the structure of the condensation product of piperylene with α-vinylpyridine will be examined in detail in the work of V. Lyudvig, and for this reason the experimental data were not presented in the paper.

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